Photocatalytic Reduction of CO_2 in Cu-doped TiO_2 Nanotubes

Jianling Meng

Tongren University, Tongren, Guizhou, 554300

Keywords: TiO_2 nanotubes; Copper doping photocatalytic reduction methane

Abstract: TiO_2 nanotubes can be fabricated by anodization, and copper doped TiO_2 nanotube composites can be obtained by electrodeposition. X-ray energy spectrum analyzers, scanning electron microscopes, and X-ray powder diffractometers were used to test the resulting material in all aspects. The results show that the TiO_2 nanotubes obtained by the anodization method have an average diameter of about 90 to 110 nanometers and an average tube length of about 300 nanometers, belonging to the anatase type; and the TiO_2 doped copper obtained by the electrodeposition method. The copper in the composite material (which is mainly composed of CUXOY/TiO_2) is mainly in the form of copper. The photocatalytic reduction of TiO_2 nanotubes made from different concentrations of $CuSO_4$ electroplating baths must be performed in a sealed, suspended photocatalytic system. Under the illumination of a 500-watt deuterium lamp, the product of the reduction of CO_2 by CUO/TiO_2 and TiO_2 is methane and carbon monoxide; under the light conditions of 6 hours, the yield of methane produced by TiO_2 nanotubes can reach 1.3x10-6/(cm^2). • h), but with 0.04 moles of copper sulfate per liter under the same conditions of CUO/TiO_2 nanotubes, the methane production can actually reach 3.7x10-6/(cm2•h), which intuitively shows the CUO/TiO_2 nanometer tube plays a very significant role in improving the photocatalytic reduction efficiency of CO_2.

1. Introduction

With the continuous development of society, the times are constantly changing, people's demand for various fossil fuels in daily production and life is showing a crazy growth trend, which indirectly leads to the CO_2 content in the air becoming More and more, the resulting greenhouse effect has become more and more serious, directly affecting the ecological balance of nature. At present, the solution to the greenhouse effect is not only to reduce the emissions of related greenhouse gases, but also to find the root cause of the problem. Resolving problems at the source is the key.

2. The Related Research and Analysis of Photocatalytic Reduction of CO_2

Chemical fixation, physical fixation, and biological paleocarbon methods are relatively traditional CO_2 treatment methods. Although they have certain effects, they have many disadvantages. For example, the conditions for implementation are relatively difficult and space is relatively effective. And the efficiency is relatively low. Therefore, many scholars began to study other treatments. Some people suggested that CO_2 could be used as part of the synthesis of small-molecule organic compounds, such as reacting with water to produce methane. This process is based on the chemical reaction mechanism using photocatalysis. In this process, the speed and selectivity of the entire reaction can be controlled by the intensity of the light and the length of the light wave [1].

Many researchers carried out a large number of experimental analysis, Zhao Yi and others studied the relevant mechanisms of photocatalytic reduction of carbon dioxide; Li Xin et al. manufactured $BiFeO_3$ and related single-wall carbon TiO_2 nanotube composite powders by sol-gel method. In this process, it was found that the photocatalytic reduction of carbon dioxide in the system synthesizes CH_3OH with approximately one-fold increase in efficiency. Compared to other forms of nano TIO_2, TiO_2 nanotubes have many advantages, such as the structure of the hollow tube, and the electron transport channels are more efficient and orderly. Because TiO_2 nanotubes are supported photocatalytic conversion materials, it not only can solve the problem of photocatalyst immobilization, making it easy to recycle, but also can be used as a photoelectrocatalyst to carry out relevant research and analysis [3]. Here, the TiO_2 nanotubes and the copper-doped TiO_2 nanotubes composite materials are mainly manufactured by anodization and electrodeposition methods. At the same time, TiO_2 nanotubes made of different concentration of copper sulfate plating solution are analyzed and studied. For the photocatalytic reduction of carbon dioxide.

3. The Main Process of the Test Analysis

The main instrument: gas chromatograph, branded Agilent.

The main reagents: lactic acid, copper sulfate, sodium hydroxide, HF; platinum electrode, graphite electrode; carbon dioxide (purity of 99.99%).

Titanium foils were first trimmed and dimensions were 40x40x0.2 (in mm) pieces, which were then processed by physical and chemical methods for polishing. 400 mL of deionized water was then charged into the plastic and stirred on a magnetic stirrer at a steady speed. Pipette 6 mL of acetic acid into the plastic cup and stir it gently. Then use a disposable plastic pipette to remove 3 mL of HF and mix it evenly. The above steps are mainly to make a mixture for the electrolyte used in the later tests. Then, the graphite electrode in the test material was used as the counter electrode, and the Ti piece was used as the working motor. The distance between the two was maintained at 40 mm, while the DC voltage supply voltage was maintained at 22 V, and the oxidation time was maintained at 25 minutes [2]. The stirring action must be maintained throughout the entire process, which ensures that the electrolyte is evenly distributed. After waiting for the reaction process to complete, remove the sample and soak it in deionized water for approximately 15 seconds, allowing it to air dry naturally. Finally, the dried Ti flakes were calcined in a muffle furnace for 3 hours, the temperature was maintained at 350 degrees Celsius, and then allowed to cool naturally to room temperature. This resulted in converted TiO_2 nanotubes.

TiO_2 nanotube composites were fabricated by electrodeposition using a three-electrode system using a platinum plate as the counter electrode, a TiO_2 nanotube for the working electrode, silver or silver chloride for the reference electrode, and copper sulphate as the plating solution. Solution () has a pH of 9. A copper-doped TiO_2 nanotube composite can be fabricated by depositing approximately 3 minutes by means of potentiostatic polarization under the action of a voltage of -0.7V. In addition, four different plating bath concentrations, 0.4/0.04/0.02/0.01 mol/L copper doped TiO_2 nanotubes, need to be prepared separately.

This experiment used a sealed-suspended photocatalytic reactor system. TiO_2 nanotubes were used as photocatalyst sheets, and they were hung on the top of the device at a distance of about 10 cm from a 500-W xenon lamp light source, and then 10 mL was added. Ionic water. Before this test was started, carbon dioxide was flushed and a buffer heater with a control temperature of 60 was added to the front of the device. After the gas is filled with the device, seal the gas pipe when the pressure becomes stable, so that the light is kept for a certain period of time, and then extract 5 mL of gas for analysis by gas chromatography [4].

The main method for the detection and analysis of the product is the gas chromatograph method. The relevant requirements for the test are: the initial temperature of the program temperature is 40 degrees Celsius, the time needs to be maintained for 5 minutes, the temperature rise rate is 12 degrees Celsius per minute, and the temperature rises to 150 degrees Celsius. After 5 minutes; import temperature requirements for the detector at 250 degrees Celsius; carrier gas purity of 99.99% for nitrogen; column flow rate of 1.0mL/min, the mode for the constant current mode; the combustion of gas using high purity hydrogen, 30 mL/min, air is 300 mL/min.

4. The Main Results of the Test Analysis

As shown in Fig. 1, SEM images of TiO_2 nanotubes fabricated by anodization are shown. The sample in FIG. a has a neat, tubular structure with uniform distribution of the Ti sheet on the surface, and no fragments of the particles appear between the two tubes, and the tube diameter ranges between 90-110 nm. It can be seen from Figure b that the length of the entire TiO_2 nanotubes is relatively uniform, about 300 nanometers in length. It can be seen from Figure c that more copper is deposited, and basically the control of TiO_2 nanotubes is blocked. It can be seen from Figure d that the copper element enters into the interior of the TiO_2 nanotubes, and the distribution is relatively uniform. It can be seen from Figure e that the deposited copper appears to be agglomerated, resulting in the inability of these large particle materials to enter the interior of the TiO_2 nanotubes, and therefore its distribution is mainly evenly distributed on the outer surface of the TiO_2 nanotubes. Figure f shows that there is basically no copper deposition on the TiO_2 nanotubes. Therefore, it can be analyzed that the effect is best when the plating solution concentration reaches 0.04 mol/L.

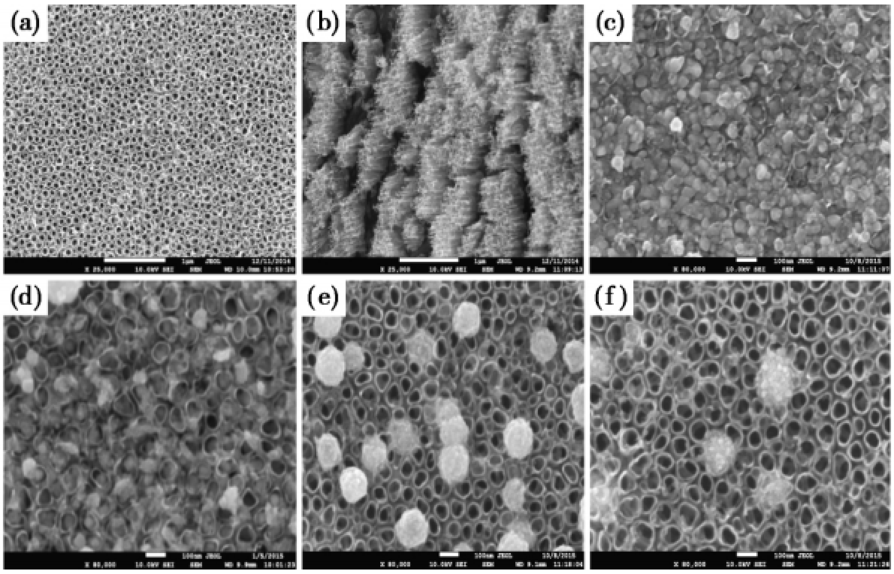

Fig.1 a and b respectively represent the cross-sections and external diagrams of TiO_2 nanotubes, and c-f respectively represent CuO/TiO_2-1、CuO/TiO_2-2、CuO/TiO_2-3、CuO/TiO_2-4

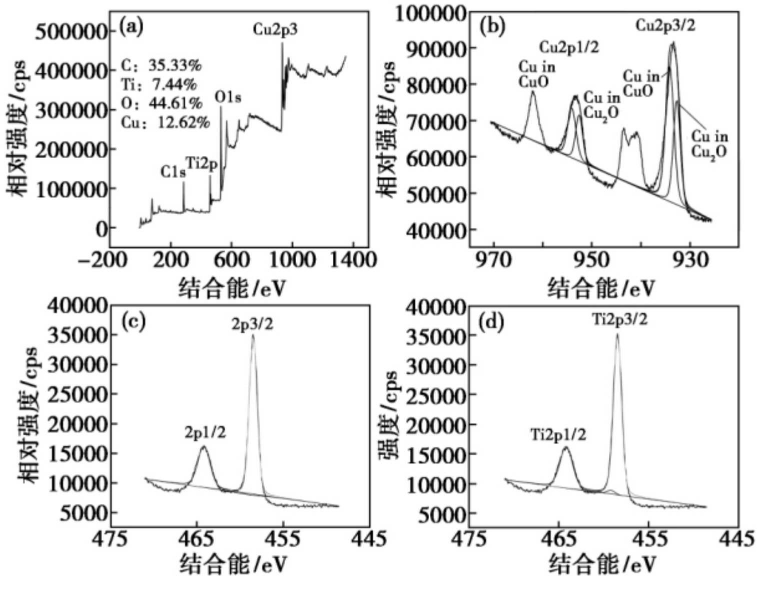

Fig. 2 a stands for TiO_2 nanotubes, b stands for Cu_2p in TiO_2 nanotubes, c stands for Ti_2p in TiO_2 nanotubes, d stands for Ti_2p in TiO_2 nanotubes

It can be seen from the XRD analysis of the composite material in Fig. 2 that diffraction peaks appear in the TiO_2 nanotubes, corresponding to 101, 103, 112, 105, 220, and 301 anatase; The TiO_2 nanotubes made by this method are of anatase type and have very good photocatalytic activity. It can be seen from the comparison chart that the diffraction peaks appear in the copper-doped TiO_2 nanotubes, indicating that the copper doping enhances the transition from an amorphous state to an anatase.

As shown in Figure 2, the XPS analysis spectrum of the test sample, a represents the type and content of elements included in the TiO_2 nanotubes, and the positions of 934.2 and 932.6 eV can be seen through the b-graph, which are the high spin of copper oxide and cuprous oxide, respectively. State binding energy, while the low spin state binding energy positions are at 954.1 and 952.3 eV, and the satellite position of the copper atom is at 962.1 eV. The binding energy can be seen in Figure c is 458.8 eV; it can be seen from Figure d that the binding energy is 458.9 eV, which is the characteristic peak of Ti element. Through comparative analysis, it can be seen that the doping amount of copper affects the Ti element, and the doping of copper element changes the bonding energy of the crystal lattice and changes to a low energy state.

During the test, carbon monoxide and methane were used as the standard sample for analysis. The peak time in the gas chromatograph was compared with the photocatalytic reduction of carbon dioxide in the above two TiO_2 nanotubes. This allowed the reduction product to be characterized. Quantitative analysis [5]. The retention time of methane and carbon monoxide standard samples in the chromatograph was 3.56 and 11.91 minutes, respectively. Then, the above-mentioned two TiO2 nanotubes were respectively placed inside a device for photocatalytic reduction reaction, and 5 mL of gas was extracted after 6 hours of illumination and placed in a gas chromatograph for examination. The two were determined based on the retention time of methane and carbon monoxide. The content of the product is analyzed, and the yield of the photocatalytic carbon dioxide product is analyzed to further analyze the actual catalytic efficiency of the above two TiO_2 nanotubes. After experimental analysis, after 6 hours of light irradiation, the yield of methane from the catalytic reduction product of TiO_2 nanotubes can be achieved, and the yield of methane from the photocatalytic reduction product is 3.4, 3.7, 2.5, and. Therefore, the presence of copper oxide can effectively increase the degree of separation of holes and electrons in the semiconductor, and it significantly improves the photocatalytic reduction efficiency of carbon dioxide. By conducting a series of light tests and then inspecting 5 mL of mixed gas, it can be seen that the production of methane and carbon monoxide will show an increasing trend with the increase of the illumination time, and the product will be produced after 6 hours of illumination. The rate will slow down, and there will be no increase after 8 hours of lighting [6].

In summary, TiO_2 nanotubes can be fabricated by anodization, and composite materials of TiO_2 nanotubes can be obtained by electrodeposition in order to enhance the material's response to visible light. Through a series of experimental verifications, copper in the TiO_2 nanotube composite obtained by the electrodeposition method can be obtained in the form of copper oxide. By using a sealed, suspended photocatalytic system, a 500 W xenon lamp is used as the light source, and the products of photocatalytic reduction of carbon dioxide in TiO_2 nanotubes and TiO_2 nanotubes are carbon monoxide and methane. Moreover, through experiments, the yield of methane produced by TiO_2 nanotubes under light irradiation for 6 hours can be achieved, and the methane production can be achieved under the same experimental conditions. It can be seen that TiO_2 nanotubes can significantly improve the photocatalytic reduction efficiency of carbon dioxide.

References

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