報告番号	甲　第　12422　号

主 論 文 の 要 旨

論文題目　**Fabrication of Fe_2O_3 Nano Architectures Based on Stress-induced Atomic Diffusion Used for Photocatalytic Water Splitting**

(応力誘導原子拡散による Fe_2O_3 ナノ構造体の作製と光触媒水分解への応用)

氏　　名　謝　毅源

論 文 内 容 の 要 旨

As a new sustainable energy source in the future, hydrogen is clean and zero emission, but the traditional method to produce it is not environmentally friendly due to the using of fossil fuels.

Solar water splitting is a new technology which can produce hydrogen using sunlight and water only. In a solar water splitting system, when the photoanode is illuminated by sunlight, the photons with an energy larger than the band gap of the semiconductor will excite the electrons from the valence band to the conduction band. The excited electrons will then move to the cathode and react with the electrolyte solution to produce hydrogen.

Fe_2O_3 is the most promising material for solar water splitting due to its suitable band gap of 2.1 eV, and the excellent stability against photo corrosion under alkaline conditions. It is the fourth most common element on Earth. However, the solar to hydrogen efficiency of the reported studies using Fe_2O_3 as the photoanode is still very low. The reasons are short excited-state lifetime, short hole diffusion length (2-4 nm), and poor electrical conductivity of Fe_2O_3.

The aim of this research is to improve the photoelectrochemical performance of photoanode by introducing Fe_2O_3 nanowire array to overcome above disadvantages. Compared to bulk materials and other nanostructures, nanowire array is believed could provide a larger surface area because of the high aspect ratio, which could not only absorb more light, but also increase the photoelectrode/electrolyte interface area, thereby enhancing the chemical reaction of water splitting. Meanwhile, the nanowire structure could reduce the diffusion distance of photogenerated minority carriers from the center to surface of nanowires because of the small diameter. Therefore, photogenerated electron-hole pairs could efficiently separate before recombination in the nanowire structure, which could eventually increase the efficiency of solar water splitting.

In this thesis, two Fe_2O_3 nanowire fabrication methods have been demonstrated, and the growth mechanisms of these two methods have also been studied. In order to improve the efficiency of solar water splitting, the relationship between the photoelectrochemical performance and the density and dimension of nanowires was investigated. The surface modification by doping several materials on the surface of Fe_2O_3 nanowires was also carried out. The details are as follows.

Chapter 1 introduces the background of this research, which includes: 1. why the clean sustainable hydrogen production method is necessary; 2. the advantage of solar water splitting; 3. several suitable materials for solar water splitting; 4. the current research of the Fe_2O_3 photoanodes used for solar water splitting.

Chapter 2 describes the experimental approaches and several principles in this study. In this chapter, the original method to evaluate the nanowire array, and the original design of the photoanode structure were introduced in detail. The evaluation methods of solar water splitting and the proposed mechanism of nanowire growth were also described.

Chapter 3 presents a new method to synthesize high density Fe_2O_3 nanowire arrays used for solar water splitting, on an iron plate, under low temperature conditions. Several experimental conditions, such as heating time, temperature, and the volume of water vapor were investigated in this chapter. It was found that with the increase of heating temperature, the average length of nanowires was increased, and the average diameter of nanowires was decreased. Nanowire array with the highest density of 14.3 wire/μm^2 was obtained at the temperature of 450 °C with 90 minutes heating. It is considered that due to the presence of water vapor, surface oxidation was promoted during the heating process, thereby enhancing the driving force induced by stress gradient due to the expansion of the oxidation layer. The largest photocurrent density (0.65 mA/cm^2) was obtained from the sample heated at 350 °C for 90 minutes, under the water vapor volume of 0.25 L/h, with the density of 8.66 wire/μm^2, the average diameter of 161 nm and the average length of 1.71 μm.

Chapter 4 reports a fabrication method to obtain the high density single-crystal Fe_2O_3 nanowire array. By polishing the surface of iron plate before heating, an extremely high density (28.75 wire/μm^2) single-crystal Fe_2O_3 nanowire array was succeeded. It is considered that the surface polishing treatment could provide a larger driving force and increase the number of weak spots on the sample surface, which lead to the increase of nanowire density. The highest photocurrent density of 0.9 mA/cm^2 at 1.23 V vs. RHE was obtained from the sample heated at 600 °C for 90 minutes with surface polishing treatment. The incident photon to electron conversion efficiency of single-crystal Fe_2O_3 nanowire (6.8% at 400 nm) is higher than that of the polycrystalline Fe_2O_3 nanowire (5.54% at 400 nm). It is considered that single-crystal nanostructure could reduce the recombination of photogenerated electrons and holes. Stability test results showed the good photocurrent response and stability of the single-crystal Fe_2O_3 nanowire photoanode, which indicates a good potential for the application of solar water splitting.

Chapter 5 compares the effect of different dopants in Fe_2O_3 nanowires. The surface modifications of the Fe_2O_3 photoanode were carried out in order to achieve a higher photoelectrochemical performance. Ti, Sn and Pt were doped on the photoanode surface by a sputtering equipment. It was found that the suitable thickness of doped material to functionalize the Fe_2O_3 nanowire array is around 10 nm, and 20 seconds of Ti doping showed a high photocurrent density of 1.94 mA/cm^2 at 1.23 V vs. RHE.

Chapter 6 is the conclusion of this thesis. In this research, a new method to fabricate high density single-crystal Fe_2O_3 nanowire array used for the photoanode of solar water splitting was proposed. With the fabricated Fe_2O_3 nanowire photoanode and Ti doped functionalization, high photocurrent density was realized for solar water splitting. The new finds of this research bring a promising potential to use solar water splitting for along term massive hydrogen production.