Preparation and Photocatalytic Properties of La$_2$CuFeO$_6$ Nanofibers by an Electrospinning Method

Gao-Feng SHI$^{1,a,*}$, Xiao CAO$^{2,b}$, Guo-Ying WANG$^{3,c}$, Xiao-Li HU$^{4,d}$, and Cheng-Ming GONG$^{5,e}$

$^1$School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou PR China

$^a$gaofengshi_lzh@163.com, $^b$632875684@qq.com

$^*$Corresponding author

Keywords: Electrospinning Method, Photocatalytic, La$_2$CuFeO$_6$ Nanofibers.

Abstract. La$_2$CuFeO$_6$ nanofibers photocatalytic material was successfully prepared by electrospinning. La$_2$CuFeO$_6$ nanofibers with an average diameter of 170 nm, which were connected to each other by rhombic La$_2$CuFeO$_6$ nanoparticles, had stable one-dimensional structure. Through the excitation of ultraviolet light and oxalic acid coupling, the La$_2$CuFeO$_6$ nanofibers as the catalyst for water-splitting reaction producing hydrogen, the average hydrogen production rate is 760.76 µmol h$^{-1}$·g$^{-1}$.

Introduction

At present, fossil fuels such as coal and petroleum are becoming more and more exhausted, and because of the fossil energy application brings more pollution, the human living environment worsens day by day, it is imminent to research new alternative energy and clean environment technology [1]. Hydrogen energy as a new energy, because of its high combustion value, combustion products without the advantages of environmental pollution, has been widely concerned [2]. The generation of hydrogen energy is diversified, in which water, biomass and other renewable materials as raw materials, the use of solar photocatalytic hydrogen production is the simplest and most efficient method [3,4]. Photocatalyst is one of the most important conditions to enhance the efficiency of photocatalytic hydrogen production [5,6]. Preparation of different photocatalysts by different preparation methods has become an important research direction [7].

The main types of photocatalyst are: (1) TiO$_2$; (2) perovskite; (3) double perovskite. The double perovskite type composite metal oxide is a kind of perovskite-type metal oxide with special crystal structure and flexible "chemical tailoring" [8]. In the perovskite type metal oxide ABO$_3$ structure, And the B-site ion is centered around the octahedron of six oxygen species [9]. In the double-perovskite-type composite oxide A$_2$B$_1$B$_2$O$_6$ structure, there are two kinds of transition metal elements in the B site, the atomic number ratio of the elements is 1: 1, and the octahedral structure of the B atom in the structure is alternated by B$_1$O$_6$ and B$_2$O$_6$. B$_1$ ion and B$_2$ ion are separated by oxygen ions to form B$_1$-O-B$_2$ structure, 6 and then showed excellent catalytic properties received by many researchers of all ages [10].

The main preparation methods of photocatalyst are: sol-gel method [11], hydrothermal method [12], liquid-hydrolytic precipitation method [13], template method, electrospinning method [14,15]. The main factors affecting the photocatalytic efficiency are the crystallinity and specific surface area of the photocatalyst. The nanocrystalline La$_2$CuFeO$_6$ with high crystallinity and high crystallinity is obtained by electrospinning. Surface area, and therefore has excellent photocatalytic efficiency.

Experimental

Put 3.0165 g polyvinylpyrrolidone (PVP) into the 30 ml of N, N- dimethyl formamide (DMF), Stir and dissolve, it and then put it on the magnetic stirrer so as to mixed more fully. Respectively
taking 1.3071 g La (NO$_3$)$_3$· 6H$_2$O, 0.2739 g Cu (CH$_3$COO)$_2$· H$_2$O, 0.2628 g Fe (CH$_3$COO)$_2$· 4H$_2$O and adding them to the above solution, stirring evenly, and getting spinning was precursor. Using the electrostatic spinning method, controlling the distance 15 cm, spinning voltage is 12.38 kV, making PVP/LCN composite nanofibers. Preoxidating the composite nanofibers 1 h under 220 °C, the heating rate of 1 °C min$^{-1}$. Then, under 700 °C, in the atmosphere of argon atmosphere 3 h, the heating rate is 2 °C min$^{-1}$, and making La$_2$CuFeO$_6$ inorganic nanofibers of different carbonization temperatures.

Fully mix the concentrated dispersion of La$_2$CuFeO$_6$ nanofibers, acetylene black and PTFE according to the rate of 85: 10:5. Add anhydrous ethanol (analysis) and get paste, smear it evenly on the nickel foam, put into the oven to dry for 4 h, and then made electrodes under 10 mpa pressure. Add anhydrous ethanol (analysis) paste, it evenly on the nickel foam, into the oven to dry within 4 h, and then made of electrodes in 10 mPa pressure. Use La$_2$CuFeO$_6$ nanofibers of electrodes assembled into a symmetry class 22 pairs of electrode system, 23, 24 in the type of CHI660B electrochemical workstation (Shanghai zhenhua instruments company) make an electrochemical performance test.

In order to better assess the electrochemical performance of double perovskite La$_2$CuFeO$_6$ inorganic nanometer fiber electrode materials under 700°C. This paper adopts the cyclic voltammograms and constant current charge and discharge method for testing.

In this paper, we had a hydrogen production experiment with a photocatalyst of pre-prepared La$_2$CuFeO$_6$. Add 0.25g La$_2$CuFeO$_6$ to 200ml 10mmol L$^{-1}$ oxalic acid aqueous solution, stir with a magnetic stirrer to make it evenly. Irradiated under a UV lamp of 365 nm for 2 hours, then measured the volume of the produced gas and calculate the gas generation rate.

Characterization

The electrospinning apparatus (Yong Kang Le Ye Co., Beijing,); TL1200 tubu furnace (Nanjing Boyunton Instrument Technology Co., Ltd.); Structure characterization of the as-prepared LiMn$_2$O$_4$ samples were performed by X-ray diffractometer (XRD, Rigaku, D/Max-2400) with Cu Kα radiation (40 kV, 150 mA, step size=0.02 ° s$^{-1}$). Data were collected in the 2θ range 10°-80° with a scan rate 2° min$^{-1}$ to obtain the diffraction patterns. The morphologies of the samples were observed by scanning electron microscopy (SEM, JSM-5600, Japan); CHI660E Electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.); Vacuum drying box (Shanghai Experimental Instrument General Factory).

Polyacrylonitrile(PAN) (Mw=150,000, were purchased from Macklin, Shanghai, China); N,N-dimethylformamide (Tianjin Kaitong Chemical Co. Ltd.); Concentrated sulfuric acid, Hydrogen peroxide(from BASF, Tianjin, China); Potassium hydrate(Laiyang Shandong double Chemical Co., Ltd.); Nickel foam (KunshanTeng Er Hui Electronic Technology Co.,Ltd); Acetylene black(Tianjin Best Union Chemical Technology Co.,Ltd); Conductive graphite (Qingdao Chenyang Graphite Company Limited); Teflon (Guangzhou Songbai Chemical Industry Co.,Ltd).

Results and Discussion

![Figure 1. Cyclic Voltammetry (CV) Curves of La$_2$CuFeO$_6$ Nanofibers.](image)
The Fig. 1 shows the $\text{La}_2\text{CuFeO}_6$ cycle volt-ampere curves. From the graph we can see, the corresponding oxides in the scanning interval, the redox peak is closer. As a result, it can be seen that there are two kinds of oxide in the CV curve, which is electrochemical reaction overlapping and becoming redox peak. At the same time, the difference between the oxidation reduction peak is pretty small. It shows that $\text{La}_2\text{CuFeO}_6$ nanometer fiber has a typical Faraday quasi capacitance characteristics and good reversibility. With the scan rate increased from 5 mv s$^{-1}$ to 100 mv s$^{-1}$, The shape of the CV curve does not change obviously, which shows that the electrode has an excellent characteristic.

![Figure 1. SEM Diagram of $\text{La}_2\text{CuFeO}_6$ Nano Fibers at 700\(^\circ\)C.](image)

The $\text{La}_2\text{CuFeO}_6$ nanometer fiber SEM made in 700\(^\circ\)C are as follows. The Fig.2 shows that fiber diameter is moderate, with an average diameter of 170 nm, have a linear space reticular structure, metal oxide $\text{La}_2\text{CuFeO}_6$ crystal shape is complete. The structure is stable and particles are spherical. The particle size is uniform distribute evenly in the fiber.

![Figure 2. SEM Diagram of $\text{La}_2\text{CuFeO}_6$ Nano Fibers at 700\(^\circ\)C.](image)

The XRD patterns of $\text{La}_2\text{CuFeO}_6$ nanofibers prepared at 700 \(^\circ\)C are shown in Fig. 3. Only a few $\text{La}_2\text{CuFeO}_6$ peaks appear in the XRD pattern in Fig.3, indicating that $\text{La}_2\text{CuFeO}_6$ is less formed and the crystal form is not completed at this temperature. $2\theta=25.8^\circ$. The crystal structure of $\text{La}_2\text{CuFeO}_6$ rhombohedral perovskite crystal was formed after carbonization at 700\(^\circ\) C, which was consistent with the (110) plane.

Through a blank contrast experiment, under the condition of no catalyst and no light, no gas generation. In our experiment, something generated. After a simple ignition test, make sure that the gas produced contains hydrogen. Due to experimental conditions, we cannot detect the specific hydrogen content, only know the gas generation rate was 760.76 \(\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}\).

**Conclusions**

The double perovskite $\text{La}_2\text{CuFeO}_6$ inorganic nanometer fiber material was made by us using electrostatic method under 700 \(^\circ\)C. The average fiber diameter is 150nm, and has a linear space reticular structure, and it is connected by diamond structure $\text{La}_2\text{CuFeO}_6$ nanoparticles. Which can produce gas under ultraviolet light, the rate of 760.76\(\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}\).
Acknowledgements

This research was financially supported by the Foundation of China (no. 21567015, 21407072 and 2016YFC0202900).

References


