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Preparation of iron oxide by electrodeposition method and its photocatalytic performance

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In this article, we prepared the metallic iron on the cathode in borate electrolyte which contains ferrous ions by electrodeposition method, and heated the iron to be iron oxide in the muffle furnace. Then analyzed the iron oxide's structural, morphological and element compositional by X-ray diffraction(XRD) and scanning electron microscopy (SEM), and also for its fluorescence analysis and light catalysis research. The results indicated that the iron oxide we prepared is given priority to ferric oxide, and contains a small amount of ferrous oxide, and it is existed in crystalline form. The morphology of iron oxide is almost appeared flake, and gathered together with irregular size, there are two crests on iron oxide's fluorescence and one renders purple light and another renders blue light, iron oxide has a good catalytic effect on the photo-degradation of organics when be used as catalyst.

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Keywords: Iron oxide, Electrodeposition, Photo-decomposition

1. Introduction

Iron, as an element, existing in the earth's crust occupies a large proportion, only ranking behind to oxygen, silicon and aluminum. It's oxide - iron oxide also named as burning limonite, rouge, iron powder etc, it's red brown powder is a crude form of pigment [1], called iron oxide red in industry [2], and it has s lot of application in paint, printing ink, rubber and other industries [3-5]. It can be used as catalyst, glass, stones, metal polishing agent [6], and also can be materials used for making iron [7].

Iron oxide is usually used as pigment because it has many colors, such as red, yellow, black, orange, brown and green. It is a kind of inorganic pigment [8], often used to color the paint, rubber, plastics, construction etc [9,10], and used as antirust pigment in the coating industry [11-14]. It can used for colorant of rubber, artificial marble, terrazzo ground, plastic, artificial leather [15,16], and it also can be used for precision instruments, optical glass polishing agent and raw material of manufacturing ferrite magnetic material and components [17,18].

There are wet method and dry method can be used for the preparation of iron oxide [19]. Wet method always used industrial iron vitriol and industrial ferrous chloride or nitrate as raw material, to prepare the ferric oxide by iron oxide precipitation method, hydrothermal method, forced hydrolysis method, colloid chemical method and so on [20,21]. The wet method crystallization products is tiny, grain soft, easier to grind [22]. Dry method is often used carbonyl iron or ferrocene as raw material, adopts the flame thermal decomposition [23,24]. Vapor deposition, plasma chemical vapor deposition method, or laser thermal decomposition method to prepare the iron oxide [25]. The dry method crystallization products is large, solid particles [26,27]. This experiment adopts the electrodeposition technology is one kind of wet methods.

Metal electrodeposition technology is one kind of the important surface engineering techniques [28]. In 1900, the silver plating technology were first put forward by professor Italian Brugnatelli, five years later, gold plating technology is put forward. Until 1840 plating technology is widely applied in industrial production, meaning the beginning of the electroplating industry [29]. So far, the plating technology's development history is more than 160 years. The electrolytic deposition of metals is an electrochemical process which can gain metals sediments(or alloys) on the cathode surface by electrolytic method [30]. Electrodeposition method has hundreds of years of theoretical and practical basis of electroplating, electrolysis and electroforming, its process is very easy to control accurately, and can prepare grain size, alloy composition and structure which are require. Also can prepare nano-composites when combined with deposition technology [31,32]. In modern industrial production, electroplating can be roughly divided into dc electroplating, plating cycle reversing electroplating, pulse plating and so on when based on the different external power [33].

In the present work, we prepared iron thin film with direct current first, then oxidated it to iron oxide under high temperature. The iron oxide thin films we have deposited using this particular method came out with monoclinic phase and showed good photocatalytic performance to degrade the methyl blue solution.

2. Experiment

All chemicals were of analytical grade and used without further purification. All the aqueous solutions were using deionized water. The experiment used iron as the anode with it’s reaction area of 20×20mm while copper was used as cathode with it’s reaction area of 20×20mm. The electrolyte composition were listed in Table 1.

Table 1. Composition and concentration of plating solution.

material composition	Concentration (g/L)
hydrated ferrous chloride($FeCl_2 \cdot 4H_2O$)	95
boric acid	5.0
saccharin	1.250
sodium fluoride	0.625
deionized water	——

The experimental steps are as follows: Frist, pretreatment of the substrate: to make the substrate polish on different specifications of the sandpaper, then make the substrate corrode 3 to 5 seconds in the mixed solution of 5ml nitric acid and 100ml anhydrous ethanol, and then used deionized water to clean it, drying it in the air. Second, configuration of the plating solution: weighed 9.5g hydrated ferrous chloride, 0.5g boric acid, 0.125g saccharin, 0.0625g sodium fluoride and then add them into the deionized water with its volume is 100ml, and make them dissolved fully. Third, electroplating process: connected iron and copper to a dc power supply, and pour the plating solution into the plating tank, and electroplate 2 hours under 5.0 V voltage, and used anhydrous ethanol and deionized water to clean the plating, get rid of the plating solution residual on the surface. Last, heat treatment process: put the plated iron in muffle furnace, keep the temperature at 900℃ for 1 hour, and cooled to the room temperature, then can be used for performance measurement and characterization.

The morphology of the iron oxide thin films were characterized by using a field emission scanning electron microscope (FE-SEM). The crystal structure was measured by using a X-ray diffract meter (XRD) (D8 Advanced XRD, Bruker AXS). The scanning speed is 6° per minute. Photo-catalytic properties were tested as followed.

Photo-decomposition test The methyl blue solution of 12 mg/L was pour into three beakers. The iron were immersed in them, and the left was used as reference. All of them were illuminated by a high pressure mercury lamp (160 W) under 15cmvertical distance. The absorbance of methyl blue solution was measured by a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan).

Fluorometric analysis Room temperature photoluminescence spectra were carried out on a fluorescence spectrophotometer (LS-55) using Xe lamp with excitation wavelength of 325 nanometer.

3. Results and discussions

In the experiment, we has carried on the performance characterization of iron oxide. Fig. 1 is XRD spectra of iron oxide, from which we can see that there are many diffraction peaks which are not the ferric oxide’s, means that the iron oxide we made in this experiment contains some other materials, we found that the mixed phase is ferrous oxide through the comparison with standard card. In the picture we can see easily that the black pentagram represents the diffraction peak of ferric oxide(α-Fe_2O_3), while the white pentagram represents the diffraction peak of ferrous oxide. Besides, we can also see that almost all of the diffraction peak’s shape is sharp, which means that the iron oxide’s crystalline is very good. And the scope of diffraction angle is from 29 degrees to 62 degrees. According to the diffraction angle and the Bragg formula, we can get the inter-planar spacing of the iron oxide and the ferrous oxide, and we can see that the crystal system of the ferrous oxide is cubic crystal system(Fm-3m) and it’s unit cell axial length is 4.29, the crystal system of the iron oxide is hexagonal system,and it’s a of unit cell axial length is 8.33 while it’s c of unit cell axial length is 24.99, and the crystal indices corresponding to the diffraction peak of ferrous oxide and iron oxide are marked on the diffraction peak.

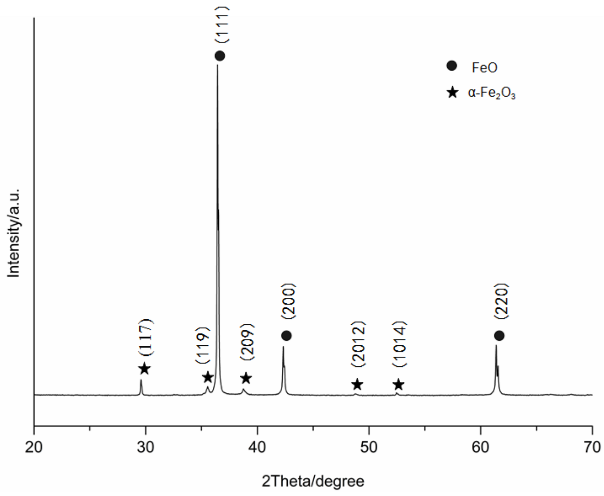

Fig. 1. XRD spectra of iron oxide.

Through the Fig. 2 we can discover easily that the iron oxide grew a dense layer of thin film on the copper plate which means that the iron’s growth condition on copper plate is very good, and there has some pittings on the surface of iron oxide, which related to the the precipitation of hydrogen in most cases. Due to the hydrogen bubble stranded on metal surface and left after the bubble grew up, which lead to the thin coating, and thick coating around it, with the result that the pitting formed. We can see that the morphology of iron oxide is almost appeared flake while the width is about 10-20μm, and gathered together with irregular size through the scanning electron microscopy picture at high magnification of iron oxide.

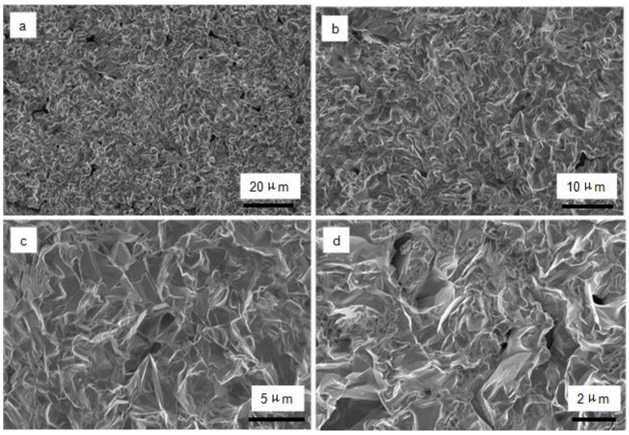

Fig. 2. Scanning electron microscopy (SEM) figure of iron oxide (a) 1k, (b) 2k, (c) 5k, (d) 10k.

The fluorescence spectra of iron oxide are measured at room temperature under the excitation wavelength of 325 nanometer with a Xe lamp. Fig. 3 shows iron oxide's fluorescence spectra, clears, the intensity is increasing when the wavelength becoming longer at the beginning, and reached a highest point while the wavelength is 452 nanometer, and then the intensity began to fall, after that the intensity increased again, and reached another crest while the wavelength is 463 nanometer, at the frist crest the wavelength is 452 nanometer which emits purple fluorescence while the intensity is 56.61 a.u., and at the second crest the intensity is 57.09 a.u. the wavelength is 463 nanometer and emit blue fluorescence. So the iron oxide emits two different fluorescences: purple fluorescence and blue fluorescence.

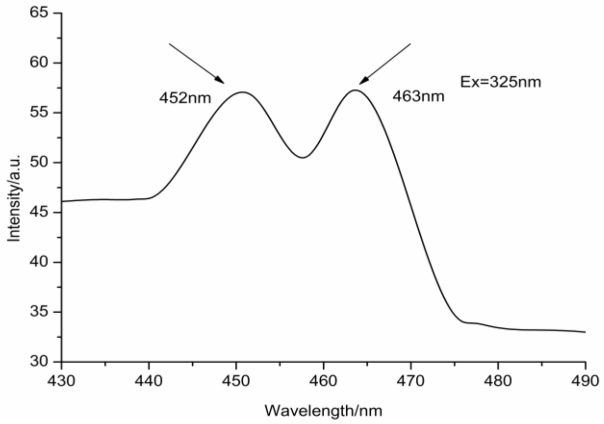

Fig. 3. The Fluorescence spectra of Iron Oxide.

From Fig. 4 shows that the rate of the photo-degradation of methylene blue under ultraviolet light with the time changing while the iron oxide be used as photo-catalyst. In the picture, the change of the rate of the photo-degradation is very quickly while the time from o to 40 minutes. And then the change become a little slower relatively from 40 to 120 minutes, and after 120 minutes there has only a little change of the photo-degradation rate until to 240 minutes, and at the 180 minutes the photo-degradation rate reached ninety percent, and then the photo-degradation rate keep above ninety percent, and the highest rate reached almost ninety-three percent, which means iron oxide has a good catalytic effect on the photo-degradation of organics when iron oxide was used as catalyst.

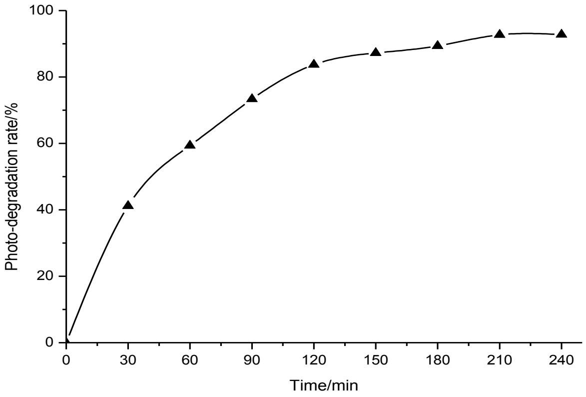

Fig. 4. The photo-degradation rate of methylene blue with the time changing when the iron oxide be photo-catalyst.

4. Conclusion

In this article, we prepare a large amount of experimental work, and finished them perfectly. Finally get some conclusions in the following through the performance characterization of iron oxide: frist, the iron oxide we prepared is given priority to ferric oxide, and contains a small amount of ferrous oxide, at the same time, the iron oxide is existed in crystalline form. Second, the iron oxide grew a dense layer of thin film on the copper plate, and the morphology of iron oxide is almost appeared flake, and gathered together with irregular size. Third, there are two crests on iron oxide's fluorescence spectra under the conditions that the excitation wavelength is 325 nanometer, and one renders purple light and another renders blue light. Fourth, iron oxide has a good catalytic effect on the photo-degradation of organics when iron oxide was used as catalyst.

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