Study on Preparation and Properties of Double Hydroxide Composite Nanomaterials

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Abstract. The purpose of this article is to synthesize a new type of visible light catalytic composite material NF@ZnO@ZnFe-LDH. In order to select a suitable LDH composed of metal ions, we selected Ni foam (NF) with a porous three-dimensional network structure as the carrier, and synthesized NF@MN-LDH composed of different metal ions by hydrothermal method (M is Divalent metal cations, N is trivalent metal cations), LDH nanosheets uniformly supported on the surface of nickel foam are obtained. Finally, the morphology characterization of the obtained object is studied.

Keywords: NF@ZnO@ZnFe-LDH, metal ion, loading.

1. Introduction

With the continuous improvement of the world economy, the problem of environmental pollution is also increasing. Among the many types of pollution, water pollution is particularly serious, which is mainly caused by the discharge of industrial wastewater. When a large amount of industrial waste water containing pollutants is discharged into rivers and lakes in nature, it not only seriously affects the natural environment, but also seriously threatens people's health. In view of the severe water pollution problem, there are currently the following treatment methods: physical adsorption, chemical degradation, microbial degradation, photocatalytic degradation technology, etc. Among them, photocatalytic technology is a kind of solar energy that can directly use nature's abundant solar energy and can efficiently remove organic pollutants in water. Therefore, photocatalytic technology is considered to be a promising water pollution treatment method. The key to photocatalytic technology lies in the development and synthesis of semiconductor photocatalytic materials with excellent performance. It uses the energy of photons to catalyze chemical reactions. In order to catalyze these reactions, the photocatalyst must efficiently absorb solar energy to generate a large number of charge carriers (electron-hole pairs), quickly separate these charge carriers to minimize recombination, and be able to strongly adsorb the reactants so that they can interact with the migrating carriers. The fluxes react and have energy and conduction band energy suitable for oxidation and reduction reaction valence bands respectively.
2. Pretreatment of nickel foam
Firstly, the nickel foam used as the carrier in the pretreatment experiment. Cut 3 pieces of foamed nickel with a length-to-width ratio of 1:2 and put them into the beaker, wash them twice with an appropriate amount of ultra-clean water, pipette 5 ml of hydrochloric acid into the beaker, add 45 ml of distilled water to dilute it 10 times. Ultrasound the nickel foam in the hydrochloric acid with an ultrasonic instrument for 30 minutes to remove the nickel oxide on the surface of the nickel foam, and then discard the dilute hydrochloric acid. After washing the nickel foam twice with ultrapure water, it was put into 50 ml of 95% ethanol and sonicated again for 30 min. Put the processed nickel foam into an oven for drying.

3. Preparation of NF@ Mn-LDH
First, prepare a dry and clean 50ml flask and add magnets to it. Weigh 0.4039 g (0.001 mol) of analytically pure iron nitrate nonahydrate, 0.5950 g (0.002 mol) of zinc nitrate hexahydrate and 0.7206 g (0.0012 mol) of urea, add 10 ml of ultrapure water and stir for 5 min to mix. Evenly. Place the flask connected to the condenser tube in an oil bath stirrer, turn on the condensed water and heat to reflux at a constant temperature of 100 ℃ for 24 h. Turn off the heat-collecting magnetic stirrer, cool the solution to room temperature, turn off the condensed water, and remove the condenser tube to obtain the ZnFe-LDH precursor. Repeat the above steps to prepare MN-LDH precursors with different metal ion components (M is +2 metal cations, N is +3 metal cations). Replace the metal salt in the reactant with other components. The feed rate is 1 : 2): (0.3751 g of aluminum nitrate nonahydrate, 0.5950 g of zinc nitrate hexahydrate, 0.4150 g of chromium nitrate nonahydrate and 0.5950 g of zinc nitrate) to obtain ZnAl-LDH and ZnCr-LDH precursors.

Put the dried nickel foam into 3 reactors one by one, and add 32 ml of ultrapure water each with a pipette. Number the reactors with No. 1~3, and add them to the No. 1 reactor. 2 ml of ZnFe-LDH precursor. Add 2 ml of ZnAl-LDH precursor to the No. 2 reactor, and 2 ml of ZnCr-LDH precursor to the No. 3 reactor, and mix them into a solution with a volume of 35 ml. The reaction kettle was placed in an oven and heated at a constant temperature of 160 ℃ for 24 h. After the reaction is over, cool the reactor to room temperature, open the reactor, transfer the solution to 3 50 ml centrifuge tubes, and name the 3 centrifuge tubes with No. 1~3 (corresponding to the reactor), and wash them with ultrapure water three times (Centrifuge at 7500 speed for 15 minutes), finally obtain pure ZnFe-LDH, ZnAl-LDH and ZnCr-LDH samples, and place them in an oven to dry. Take out 3 pieces of foamed nickel in turn, put them into 3 15ml centrifuge tubes, add an appropriate amount of ultrapure water and sonicate for 5 min and repeat twice to obtain NF@ZnFe-LDH, NF@ZnAl-LDH and NF@ZnCr-LDH samples. Place in an oven for drying.

4. Preparation of NF@ZnO@ZnFe-LDH
The preparation of NF@ZnO@ZnFe-LDH is mainly divided into two steps. The first step is to prepare NF@ZnO by electrodeposition. The second step is to load ZnFe-LDH on the surface of NF@ZnO by hydrothermal synthesis to obtain NF@ZnO@ZnFe-LDH.

4.1. Preparation of NF@ZnO by electrodeposition
2.59 g Zn(COOH)2 (0.017 mol) and 4.958 g Zn(NO3)2•6H2O (0.017 mol), make a 100 ml solution with a volumetric flask. In the three-electrode system (the counter electrode is a platinum wire, the reference electrode is a calomel electrode, and the working electrode is a nickel foam) first apply -1.3 V voltage, energize at 85 ℃ for 10 s, and then apply -1 V voltage for 200 s, Deposit twice to get NF@Zn(OH)2. Take out the foamed nickel and dry it, and calcinate it under the protection of argon at 350 ℃ for 1 h (heating rate is 2 ℃/min), and finally NF@ZnO is obtained.

4.2. Preparation of NF@ZnO@ZnFe-LDH
Put the prepared NF@ZnO into the reactor, use a pipette to transfer 32 ml of ultrapure water and 3 ml of ZnFe-LDH precursor into the reactor, and mix them into a 35 ml solution. The reaction kettle was
placed in an oven and heated at a constant temperature of 160 °C for 24 h. After the reaction is over, cool the reactor to room temperature, open the reactor, take out NF@NiFe-LDH, put it in a 15 ml centrifuge tube, add an appropriate amount of ultrapure water, and ultrasound for 5 min. Repeat twice to obtain pure NF@NiFe-LDH, Place it in an oven for drying.

4.3. NF@ZnO@ZnFe-LDH Photocatalytic Degradation of Acid Red 1 Experiment
First prepare 500 ppm acid red 1 solution, measure 0.05 g of acid red 1 and use a 100 ml volumetric flask to prepare a 500 ppm acid red 1 solution, then pipette 500 ppm of acid red 1 solution for use Transfer 10ml to a 100ml volume and dilute it 10 times to obtain a 50 ppm acid red 1 solution. Pipette 50 ml of Acid Red 1 solution into two 100 ml beakers, add 12 slices of NF@ZnO@ZnFe-LDH and NF@ZnO to the solutions in the two beakers, and then stir for 30 min in the dark Adsorption (basically reach equilibrium). After the solution reached equilibrium, 3 ml of the solution were taken as samples from the two sets of beakers. After the sampling is completed, start the photocatalysis test, irradiate the solution with a xenon lamp, and then take samples every 10 minutes until the acid red 1 dye in the flask containing NF@ZnFe-LDH is almost completely degraded and the liquid becomes clear Transparent. The UV-Vis spectrophotometer is used to measure the absorbance intensity of the residual acid red 1 in the aqueous sample, and the concentration of the residual acid red 1 dye molecule in the corresponding sample is calculated from the standard concentration working curve, and the photocatalytic degradation curve is drawn based on the result Figure.

5. Morphology characterization of NF@MN-LDH
It can be seen from the SEM image (Figure 1) that the LDH composed of different metal ions can be uniformly loaded on the foamed nickel and present a flake shape. Compared with pure LDH powder, this morphology has a significantly improved specific surface area, which can provide more contact area and catalytic active sites for pollutant molecules as a photocatalytic material for adsorbing and degrading pollutants. The morphology of LDH composed of different metal ions also has a certain change. In contrast, NF@ZnFe-LDH has the thinnest nanosheets and the most abundant pore structure.

Figure 1. SEM photo of NF@MN-LDH (the left column is the enlarged image, the right column is the full view)
6. Morphology Characterization of NF@ZnO@ZnFe-LDH

We synthesize NF@ZnO@ZnFe-LDH in two steps. From the SEM photo in Figure 4, we can see that the ZnO loaded on the surface of the nickel foam by electrodeposition also presents a porous nanosheet shape, and the distribution is relatively uniform. Furthermore, the ZnFe-LDH loaded by the hydrothermal method still maintains the morphology of the nano flakes, is closely combined with the ZnO nano flakes, and is evenly distributed on the surface of the nickel foam. NF@ZnO@ZnFe-LDH presents a network hole structure formed by staggered stacking of nanosheets, with a large specific surface area. This provides very favorable conditions for its subsequent adsorption and degradation of pollutant molecules in the water.

![Figure 2. SEM photos of NF@ZnO and NF@ZnO@NiFe-LDH](image)

7. Conclusion

In this thesis, a new type of visible light catalytic composite material NF@ZnO@ZnFe-LDH was synthesized based on zinc oxide and hydrotalcite-like (LDH). The ZnO loaded on the surface of the nickel foam by the electrodeposition method is in the shape of porous nanosheets, and the distribution is relatively uniform, and the ZnFe-LDH loaded by the hydrothermal method maintains the morphology of the nanosheets, and is tightly combined with the ZnO nanosheets, and is evenly distributed on the surface of nickel foam.

Acknowledgements

"Design, R&D, and Marketing Promotion of an Intelligent Tea Drinking Service Robot" (GIJ181064), the 2018 Jiangxi Provincial Department of Education Science and Technology Project; "A remote multi-person intelligent cloud platform based on VR/AR technology" (201913421001), 2019 National College Student Innovation Training Program Project of the Ministry of Education; Nanchang City VR Innovation Development and Application Key Laboratory Project Fund (2018-NCZDSY-001).

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