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Preparation of Graphene and Nano-Nickel Oxide Composite Electrode and Its Application in Photoelectrically Coupled Water Hydrogen Production

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ABSTRACT

In today's world, fossil fuels are facing energy shortages and environmental pollution, so the focus is on green and clean energy sources such as hydrogen, and electrolysis of water to produce hydrogen has become a highly anticipated method of hydrogen production. This paper mainly focuses on the development process of graphene composites in water hydrogen production technology, reviews the research results of electrolytic water hydrogen production technology and photoelectric coupling hydrogen production technology at home and abroad, critically evaluates the strengths and weaknesses of existing research, points out the limitations and research gaps of materials, and analyzes the research progress of graphene-nickel oxide composite electrodes in photocatalysis and electro catalysis performance. This paper elaborates on the hydrogen production principles, technical difficulties and improvement directions of its application in photo coupled water hydrogen production, and further analyzes its potential and feasibility as a bifunctional catalyst, providing new development ideas and methods for future green hydrogen production technology.

KEYWORDS

Graphene composites; Transition metal oxides; Photoelectric coupling technology; Green water hydrogen production technology

1 Introduction

The International Energy Agency released a comment that by 2030, green hydrogen production capacity will increase significantly, but high costs remain the biggest obstacle to marketization. Electrolysis of water for hydrogen production has become a widely concerned hydrogen production technology among researchers. Traditional hydrogen production technologies are expensive, energy-consuming and inefficient. The two half-reactions of electrolysis of water for hydrogen production, hydrogen evolution reaction and oxygen evolution reaction, are both limited by the performance of catalysts and the way of energy input. The current traditional catalysts have limitations such as high cost of precious metals, limited catalytic efficiency, poor stability, and complex and difficult preparation process, which are not conducive to marketization. Therefore, the development of low-cost, low-energy-consumption and high-activity bifunctional electrocatalysts is of great significance for the practical industrial application of electrolysis of water for hydrogen production. The innovation of graphene nickel oxide composite electrode lies in its bifunctional catalytic activity and the performance of photoelectric coupling water splitting for hydrogen production.

The 19th National Conference on Catalysis of the Chinese Chemical Society [1] proposed that graphene materials have great potential for development and application in the field of photo electrocatalytic water splitting. The unique two-dimensional layered structure of graphene endows the composite material with excellent catalytic performance. The number of layers, lattice orientation, defect degree, nanostructure, etc. affect its electronic structure, but easy and precise control has become the direction of continuous efforts by researchers. Nickel oxide nanomaterials are low-cost and NiO itself has catalytic activity for the oxidation of water (OER：Oxygen Evolution Reaction), which enhances the absorption intensity of the electrode in the visible light region, good electrical conductivity and low cost. Graphene, with its high specific surface area, excellent electrical conductivity and mechanical strength, is an ideal catalyst carrier. Graphene can be used as a co-catalyst to provide more active sites. Thus, it has excellent catalytic oxygen evolution performance. The P-type properties of NiO combine with the high electrical conductivity of graphene to form heterojunctions [2]. The high carrier mobility of graphene can accelerate electron transport and reduce recombination loss. The enrichment of electrons and holes on different conductor surfaces promotes the separation of photogenerated electron-holes, thereby reducing the probability of recombination and thus having high photocatalytic hydrogen production activity. In this way, the graphene-nickel oxide composite electrode has catalytic function for both hydrogen and oxygen evolution reactions, promising to achieve dual-function catalytic electrolysis of water for hydrogen production [3], greatly freeing the energy input mode and further improving the hydrogen production efficiency at a low cost. This paper attempts to propose the feasibility of a new composite electrode material, graphene nickel oxide nanomaterial, as a bifunctional(ORR：Oxygen Reduction Reaction/OER) electrocatalyst by integrating the current research status of graphene-based composite electrodes in electrocatalytic water hydrogen production, photo electrocatalytic water hydrogen production and bifunctional electrocatalytic water hydrogen production at home and abroad, providing a direction for further research on low-cost, low-energy and high-efficiency water hydrogen production.

2 Application of graphene in catalytic electro catalytic hydrogen production

2.1 Current status of electrolytic water hydrogen production technology

Electrolysis of water to produce hydrogen and oxygen directly through electrical energy is the earliest and most typical green hydrogen production technology. This technology is divided into alkaline water electrolysis, proton exchange membrane water electrolysis and solid oxide water electrolysis. At present, OER electro catalysts are mainly composed of expensive and limited precious metal platinum-based electro catalysts or ruthenium, which not only have high costs but also have problems of difficult agglomeration with other nano materials. The properties of graphene, such as high electrical conductivity and large specific surface area, can be combined with traditional metal materials of other elements to achieve higher OER electro catalytic activity.

2.2 Graphene transition metal composite catalyst

The preparation of graphene-metal composites is mature and there are many studies in electro catalytic chemistry applications. In particular, transition metal elements and oxides [1] are green, safe, inexpensive and readily available. When combined with graphene, they have considerable bifunctional activity and good stability in hydrogen and oxygen evolution, and have great potential compared to noble metal bases.

Ni [4], as a low-cost transition metal, has long been used by researchers as a non-precious metal cathode hydrogen evolution material. To maintain the activity and stability of the anode oxygen evolution material, Ni-doped alloy catalysts are also used as anode electrodes. From the current studies on the electrochemical performance of graphene-nickel oxide composites, the preparation technology of graphene-nickel oxide composites is also relatively mature. Chen Si used microwave method [5] to rapidly prepare composites and concluded that NiO nano materials have a complete lattice structure. Since positively charged Ni can combine with negatively charged oxygen-containing functional groups on the surface of graphene through electrostatic attraction and coordination, the combination of graphene and nickel oxide is very tight. Liu Jinxing combined NiO nano rods with graphene sheets using the hydrothermal method [6], and the preparation process is environmentally friendly and has great application potential. The reduced graphene oxide-nickel oxide composite electrode has a large surface area and appropriate mesoscale porous size, as well as a stable structure, which enables the electrolyte ions to fully contact the electrode material for efficient electrochemical reactions. Ji Qizhe [7] prepared graphene by combining ball milling and CVD methods and uniformly decorated NiO and Ru nanoparticles on graphene nano sheets, and successfully prepared multiple composite structures. The combined effect of NiO and Ru gave the composite superior OER electro catalytic activity, which could serve as a potential alternative to noble metal catalysts. Transition metal nickel itself is also a material with great potential for development in the field of catalysis, and many researchers have studied nickel-based nano materials, Ma Mengyao [8] NiMoP nano materials with NiP/NiMoP2 hetero junctions exhibit excellent hydrogen evolution catalytic activity in both acidic and alkaline conditions, A halogen-doped single-atom composite catalyst was prepared by electrochemical deposition, and it was found that the I-Pt/Ni(OH)2 catalyst has better mass activity than commercial Pt/C.

3 Graphene composites photocatalytic hydrogen production

3.1 Selection and Preparation of Photo-coupled Catalysts

When photo catalysts are used alone, the catalytic effect is limited by factors such as the activity of the photocatalyst and the reaction conditions. Commonly used catalysts are semiconductor materials. When light shines on semiconductor materials, electrons are excited to form electron-hole pairs. Electrons participate in the reduction reaction while holes participate in the oxidation reaction and oxygen precipitation reaction. In the presence of water, electrons can reduce hydrogen ions in water molecules to hydrogen gas, and holes oxidize water molecules to produce oxygen gas. (OER) electro catalysts are typically precious metals such as platinum, cobalt, manganese, nickel, etc. Scientists have been exploring alternative materials to reduce energy consumption and cost, and current research has found that combining photo electro catalysis with other technologies, such as metal-organic framework photo electro catalysis coupling system (MOF-PEC), can make up for this deficiency. Hetero structures can be prepared by combining metal oxides, metal hydroxides (Ni(OH)2, Co(OH)2, Fe(OH)2), perovskite materials, etc. through low-temperature reflux [9], and their photocatalytic performance can be enhanced through synergistic effects.

3.2 Research status and deficiencies at Home and abroad

In 1972, Fujishima et al [10]. first achieved solar photo electrochemical water splitting using TiO_2 photo anodes and Pt electrodes. Researchers at home and abroad have paid extensive attention to graphene-semiconductor composite photo catalysts, and TiO2 has also become a research hotspot for researchers. Yang Minquan [11] prepared graphene-TiO2,carbon nanotube-TiO2 and fullerene-TiO2. The study found that graphene has a more significant effect and performance in enhancing the catalytic activity of semiconductor photo catalysts compared with carbon nanotubes and fullerenes, which shows the unique and excellent properties of graphene itself. In addition, metal-organic framework compounds (MOFs) have excellent properties similar to zeolites and have good commercial prospects in many fields such as adsorption separation and catalysis. Photocatalyst materials derived from them have achieved good research results in the field of photocatalytic water splitting for hydrogen production [10]. Lin et al. reported a CdS/NiO hetero junction photocatalyst derived from MOOF, with a hydrogen production rate of 7.1.2 m m o l under ultraviolet light, which was increased to 14.2.5 m mo l after surface modification with polyvinylpyrrolidone (PVP). Li et al. prepared NiS/CdS/TiO $_2$ composite photocatalyst materials using MOF as a template, and the composite catalyst showed the highest catalytic activity when CdS content was 30% and NiS content was 0.3%. TiO2, as a research hotspot, can be combined with graphene through electrodeposition technology, sol-gel technology, etc. Carreno-Lizcano et al [12]. prepared N-fGO/TiO2 electrodes, and Zhang Zeyang et al [13]. used TiO2NTs as cathode and GO dispersion as electrolyte to directly reduce GO to rGO on TiO2NTs by pulsed electrodeposition, both indicating an increase in electron transport rate. It can be seen that the preparation technology of graphene composite electrodes is relatively mature, but the above catalytic electrodes have characteristics such as low response to visible light, easy and rapid recombination quenching of photo generated electrons and holes, and low catalytic efficiency. Later, semiconductor materials such as metal oxides, sulfides, nitrogen oxides and non-metallic graphite phase carbon nitride were widely used in photocatalytic water splitting for hydrogen production. Wan Xingchen [14] et al. used two-dimensional material graphene oxide and metal-organic framework compound ZIF-67 as precursors. A three-dimensional cross-linked graphene-loaded CoO nanoparticles composite catalyst material was prepared by solvothermal reaction and high-temperature calcination. The study found that the composite material demonstrated excellent photocatalytic water splitting and hydrogen production performance in the full spectrum, single-wavelength ultraviolet light, and single-wavelength visible light, but the preparation cost was still high and the difficulty was high, and the generalization was not strong. Lu Kangqiang [9] synthesized transition metal hydroxides such as Ni(OH)2, Co(OH)2,Fe(OH)3 and Cu(OH)2 using graphene as a template by low-temperature reflux. The experiment found that the Ni (OH)2 nano sheet array -10%GR composite material has excellent photocatalytic activity for CO2 reduction. Commercial Elicarb graphene (EGR) was combined with CdS semiconductors to produce CdS- EGR composites with tighter interfaces.

4 Feasibility of graphene-nickel oxide composite electrode bifunctional catalysts

4.1 Selection and preparation of bifunctional catalysts

Bifunctional catalyst is a catalyst with two different functional catalytic properties, which can simultaneously optimize the hydrogen and oxygen evolution reactions in water hydrogen production applications and achieve efficient water electrolysis for hydrogen production. It is usually a metal-organic framework catalyst with a bimetallic center. Yang Minquan, previously mentioned, studied the preparation of graphene-CDS-TiO2 ternary composite photo catalysts using graphene TiO2 as a dual co-catalyst [11]. Due to the formation of multi-level electron transport paths within the ternary composite, photo generated electron-hole pair separation could occur under light, further enhancing the photocatalytic activity of the composite. Ma Chenchen designed and studied the mechanism of bimetallic and trimetallic active center doped graphene M-N-C type bifunctional electro catalysis based on the first principles of density functional theory [15], mainly discussing the transition metal and nitrogen co-doped graphene catalyst Using the M-N-C catalyst structure composed of Fe, Co, and Ni, it was found that each metal site has the potential to become an active site. Li Xiangyi also prepared the transition metal/heteroatom co-doped carbon-based catalyst FeCo/N-C using transition metals and phenoline-imidazole derivatives as complexes [16], selected the appropriate preparation template, Promote pyrolysis to obtain the products, and then investigated their electrocatalytic properties and applied them to zinc-air batteries. The study found that FeNi/NS-C electrocatalyst is an excellent ORR/OER bifunctional electro catalyst. Its multi-component and multi-active center synergistic effect provides high catalytic activity, and it has high stability and can maintain high catalytic efficiency even after long charge and discharge.

4.2 Feasibility of graphene-nickel oxide composite electrode for bifunctional catalysis of water hydrogen production

The potential and superiority of graphene-nickel oxide composites as bifunctional catalysts lie in the fact that we conducted experiments on NiO nano flowers and found that they have catalytic activity for oxygen evolution in water, and the preparation of NiO nanoparticles is simple and rapid. We also found that co-doped NiO materials have good catalytic activity for the oxygen evolution reaction in electrolyzed water. The application fields such as photoelectric coupling technology have gradually expanded. Catalytic electrodes have changed from only having catalytic activity under ultraviolet light irradiation to generating catalytic activity under full-spectrum visible light and ultraviolet light irradiation. Nickel oxide nano materials have low cost and NiO itself has electro catalytic activity for the oxidation reaction of water (OER), which enhances the absorption intensity of the electrode in the visible light region and has good electrical conductivity. Low cost, and graphene, with its high specific surface area, excellent electrical conductivity and mechanical strength, is an ideal catalyst carrier. Graphene can act as a co-catalyst, providing more active sites and thus having excellent catalytic oxygen evolution performance.

Modification and reduction of NiO to Ni or direct compounding of Ni can form heterojunctions with graphene, achieving more efficient photo electro catalysis. Huang Minghui [17] combined Fe2O3 with NiO and investigated their hydrolysis performance. Using the simplest and fastest microwave deposition method, a Fe2O3@NiO composite catalyst was constructed on carbon cloth (CC). Structural characterization and DFT calculation revealed that the reconstructed Ni/Ni (OH) 2 had higher catalytic activity and excellent stability for water splitting. The chemical deposition method was used to prepare Ni/NiO-2/CC to produce the optimal catalyst.

4.3 Catalytic mechanism and mechanism of the catalyst

Based on the literature, the possible photoelectric coupling processes of graphene-nickel oxide composite electrodes can be inferred and summarized [2]:

(1) Light absorption: When the semiconductor photocatalyst, namely the nickel-oxide-graphene composite electrode, is exposed to external light with an energy equivalent to or higher than the band gap energy, electrons in the valence band will absorb energy and transition to the conduction band, while holes are produced in the valence band, thereby generating photo generated electron-hole pairs.

(2) Separation and transfer of photo generated charges: The generated photoelectrons and holes partially recombine due to collisions, defects, etc., while the unreorganized photoelectrons and holes migrate to the surface of the semiconductor material, that is, the photoelectrons transfer from the conduction band of NiO to graphene, while the holes remain in the valence band of NiO.

(3) Interfacial reactions: Active electrons that migrate to the surface of the semiconductor participate in the reduction reaction, while holes participate in the oxidation reaction. For photo electro catalytic water splitting to produce hydrogen, in most cases, the P-type semiconductor material, NiO, is used as the photocathode hole to drive the oxidation reaction of water, and the electrons on the graphene surface drive the oxygen evolution reaction. The P-type property of NiO combined with the high electrical conductivity of graphene can form an in-built electric field that promotes the separation of photo generated electron-hole pairs. The high carrier mobility of graphene can accelerate electron transport and reduce recombination loss. The enrichment of electrons and holes on different conductor surfaces promotes the separation of photo generated electron-holes, thereby reducing the probability of recombination and thus having high photocatalytic hydrogen production activity.

5 Conclusion

This paper, by reviewing the shortcomings of graphene in the application of catalytic water electrolysis and photoelectric coupling water hydrogen production, discovers that the cost and stability of noble metal electrodes are poor, and the preparation technology of some overly advanced materials combined with graphene is difficult and complex. The development of low-cost non-noble metal catalysts such as nickel oxide graphene nanomaterial electrodes can solve the problem. Through the review and organization of literature, the maturity of its preparation methods is found, and the mechanism of photoelectric coupling of composite electrodes and the feasibility of bifunctional catalytic electrodes (ORR/OER) are analyzed. The combination of graphene and low-cost transition metal nickel oxide reduces the cost of hydrogen energy production. The composite electrode with both photocatalytic and electrocatalytic properties breaks the limitation of single function, combines photocatalysis and electrocatalysis, and significantly improves the efficiency of water hydrogen production. The combination of p-type semiconductors and graphene reduces the recombination of electron-hole pairs, thereby improving the efficiency of both hydrogen evolution and oxygen evolution reactions. The interdisciplinary intersection of materials science, catalytic chemistry, and clean energy technology provides innovative ideas for future scientific development. The challenges to be overcome and future research directions are the optimization of the interface stability between graphene and nano-nickel oxide and how to scale up the production of composite electrodes. It is hoped that this paper can provide references and directions for future research on low-cost and low-energy graphene in photoelectric coupling water hydrogen production.

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