

Anode modified by BiFeO₃ and application in resourceful treatment of salty organic wastewater

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The Ni foil or fluorine-doped SnO₂ transparent conductive glass substrates modified by BiFeO₃ film with a different atomic ratio of Bi to Fe were prepared by the method of spin coating-calcination at a different temperature. Coupling photo-catalysis with electro-catalysis, resourceful treatment of salty organic wastewater containing methyl orange and cadmium ion was proposed and experimentally achieved. Under visible light irradiation, the highest H₂-production rate (5.46 ml/h cm²), degradation efficiency of methyl orange (51.6%), and the recovery precipitation weight of cadmium hydroxide (0.1846 g) were obtained with Ni foil modified by BiFeO₃ (Bi:Fe = 1.10:1.00) film at 550°C of calcination. X-ray diffraction, ultraviolet–visible diffuse reflectance spectroscopy, scanning electron microscopy, and the resourceful treatment test of salty organic wastewater were used to characterise the catalyst film.

1. Introduction: Energy crisis and water pollution are urgently needed to solve. The rapid consumption and environmental pollution of fossil fuels such as coal and petroleum make people urgently to find new clean energy, and hydrogen has been widely studied as a kind of highly efficient and clear energy carrier [1, 2]. Meanwhile, it is urgent to develop new methods to deal with wastewater, especially intractable salty organic wastewater.

The application of water electrolysis to produce hydrogen and electro-catalytic oxidation of organic wastewater is limited because of high electric power consumption [3–6]. Also, there are also some problems with photo-catalytic water splitting to produce hydrogen and photo-catalytic degradation of wastewater, such as poor use of visible light and low light quantum efficiency [7–10]. In order to suppress the recombination of photo-generated carriers to improve the efficiency of the photo-catalysis, it is reasonable to construct the photo-electro-chemical process by applying a bias voltage of <0.8 V generally. Also, in order to reduce the power consumption of electrolysis and electro-catalytic process, the photo-electro-catalytic process is carried out by modifying the anode with a photo-catalyst and irradiating the anode with light to convert the light energy directly into the chemical energy [11].

Salty organic wastewater is the suitable electrolyte of the photo-electro-catalytic process, and the key to the resourceful treatment is the anode modification by photo-electric-catalytic materials. It is well known that TiO₂ is a representative of the photo-catalyst and has been widely used in the field of photo-catalysis. However, its application has been limited due to the wide band gap, high recombination efficiency of carriers and other inherent defects [12].

As a new kind of semiconductor photo-catalyst, BiFeO₃ with a perovskite structure is a typical representative photo-catalyst [13]. Having a narrow band gap about 2.2 eV, good charge mobility and excellent absorption properties of visible light [14], BiFeO₃ is an ideal photo-catalyst for water electrolysis assisted by visible light to produce hydrogen and photo-catalytic degradation of organic pollutants.

Our work was based on the industrial alkaline water electrolysis technology, the anode was modified by BiFeO₃ film, and salty organic wastewater was used as the electrolyte instead of sodium hydroxide. Coupling photo-catalysis with electro-catalysis and the resourceful treatment of salty organic wastewater was experimentally achieved. The degradation of organic pollutants, recovery

of heavy metal ions, and hydrogen production take place at the same time in the suggested process of resourceful treatment of salty organic wastewater.

2. Experiment

2.1. Characterisation: Crystallographic information of the obtained samples was observed using a powder X-ray diffraction (XRD, D/max 2550 V, Rigaku Tokyo, Japan). The morphology and size were examined using an S-4800 scanning electron microscope (SEM, JEOL Tokyo, Japan). The light absorption properties of the samples were tested using a Cary 500 ultraviolet–visible (UV–Vis) spectrometer (Varian, American).

2.2. Preparation of BiFeO₃/Ni [fluorine-doped SnO₂ (FTO)]: The Ni or FTO substrates modified by BiFeO₃ film were prepared by the spin coating-calcination method.

Preparation of BiFeO₃ precursor: According to the atomic ratio of Bi to Fe = 1.00:1.00, 1.05:1.00, and 1.10:1.00 and the total concentration of bismuth and iron of 0.3 mol/l, bismuth nitrate pentahydrate and iron nitrate nonahydrate were dissolved completely into the mixed solvent of 1:1 volume ratio of ethylene glycol monomethyl ether to acetic acid. The BiFeO₃ precursor was obtained after the aging process of the mixed solution at room temperature for 24 h.

Film coating: First, the Ni or FTO substrates were ultrasonically cleaned by 30% sodium hydroxide solution and acetone/ethanol mixed solution successively. Second, Ni or FTO substrate was spin coated by BiFeO₃ precursor by using an intelligent program-controlled glue machine (Jinglin KW-4B) with a spin speed of 2000 r/min for 25 s. Then Ni or FTO substrate was dried in an oven at 150°C for 15 min. After cooling down to room temperature, the Ni or FTO substrate was heated up to 350°C for 10 min in a muffle furnace at a heating rate of 10°C/min. After cooling down to room temperature, the above-mentioned spin coating and heat treatment process was repeated four times. The samples of BiFeO₃/Ni(FTO) were prepared by calcination under different temperatures (450, 500, 550, and 600°C) for 60 min at a heating rate of 5°C/min from 350°C.

2.3. Resourceful treatment of salty organic wastewater: A schematic diagram of the experimental facility is shown in Fig. 1. It was based on the H-type electrolytic cell of water electrolysis.

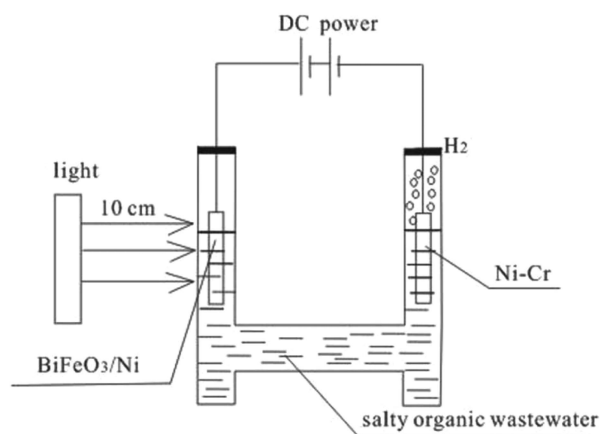


Fig. 1 Experiment facility schematic diagram

The simulated wastewater containing Cd^{2+} (2.00 g/l) and methyl orange (20.0 mg/l) was used as an electrolyte with 10% sodium chloride to increase the conductivity. The anode was Ni modified by BiFeO_3 film and the cathode was Ni-Cr and the anode was irradiated with UV (150 W high-voltage mercury lamp) and visible light (1000 W tubular xenon lamp placed in annular tube cooled by water), and the electrolytic cell voltage was 2.0 V.

The H_2 evolved from cathode was analysed by gas chromatography (Zhejiang Fuli Instruments Co. Ltd), using high-purity nitrogen as a carrier gas and a thermal conductivity detector [11]. The mixed gas containing hydrogen and air from the cathode area was sampled by a micro-injector and analysed by gas chromatography, and the rate of hydrogen production was calculated.

The degradation efficiency of methyl orange in the electrolyte was analysed by determination of the absorbance at the main absorption wavelength of 468 nm after the electrolyte was centrifuged. The absorbance of electrolyte without treatment was recorded as A_0 , and the absorbance of the electrolyte after treatment was recorded as A , so the photo-electro-catalytic degradation efficiency of methyl orange in the wastewater was expressed as $(A_0 - A)/A_0$.

The removal and recovery of cadmium ions in the electrolyte were characterised by the weight of the dry precipitate of cadmium hydroxide after the electrolyte was filtered by filter paper and washed by pure water.

3. Results and discussion

3.1. X-ray diffraction (XRD): Fig. 2a shows the XRD patterns of the film ($\text{Bi:Fe} = 1.10:1.00$) on Ni substrate at different calcination temperatures. It can be seen from Fig. 2a that the sample has no distinct diffraction peaks of BiFeO_3 <400°C. As the calcination temperature increased, the distinct peaks of BiFeO_3 were observed, but there is a significant amount of other phases. It is well known that other phases including Bi_2O_3 and $\text{Bi}_{25}\text{FeO}_{40}$. The crystal phase was changed from BiFeO_3 to $\text{Bi}_{25}\text{FeO}_{40}$ at 600°C and accompanied by a small number of impurity peaks of BiFeO_3 and Bi_2O_3 . In [15], the reason for the formation of various types of impurity phases including $\text{Bi}_{12}\text{Fe}_4\text{O}_9$, $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$, $\text{Bi}_3\text{Fe}_4\text{O}_9$, and Bi_2O_3 could be explained on the basis that Bi(III) in acidic solution undergoes intramolecular polycondensation of hydrate ions.

Fig. 2b shows the XRD patterns of the film ($\text{Bi:Fe} = 1.00:1.00$, 1.05:1.00, and 1.10:1.00) on Ni substrate calcined at 500 and 550°C. When the amount of bismuth overdosed 10% to the stoichiometry of BiFeO_3 and the calcination temperature was raised to 500°C, strong characteristic peaks of BiFeO_3 were obtained and impurity peaks reduced substantially. There were highly crystalline and the more pure perovskite phase of BiFeO_3 (JCPDS Card No.

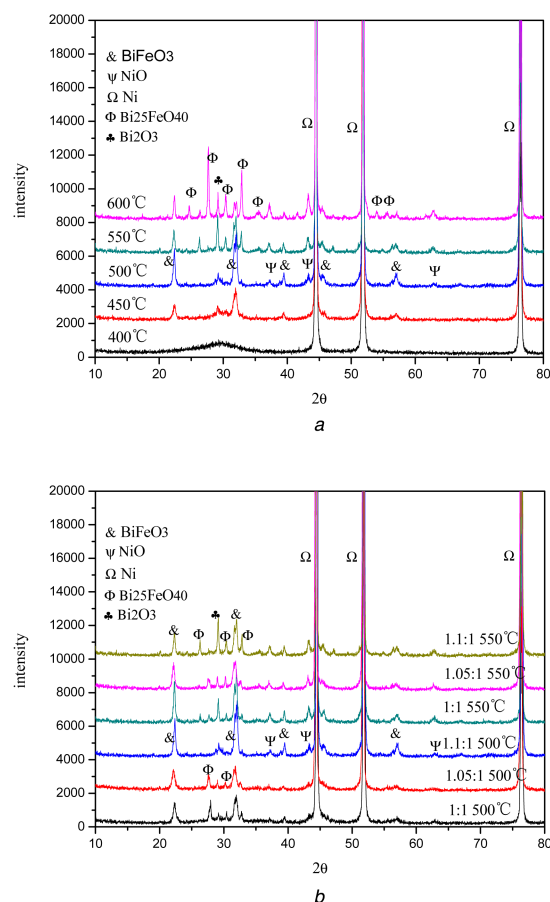


Fig. 2 XRD patterns of the prepared samples at a different atomic ratio of Bi to Fe and calcination temperature

86-1518) [16]. The diffraction peaks obtained could be indexed to the hexagonal structures of BiFeO_3 , which are in good agreement with literature results [16]. As the calcination temperature was raised to 550°C, there were strong characteristic peaks of BiFeO_3 accompanied by a small number of impurity peaks of $\text{Bi}_{25}\text{FeO}_{40}$ and Bi_2O_3 .

At the same time, the peaks of 37.18°, 43.12°, and 62.44° confirmed the presence of NiO above 500°C. Also, the peaks of 44.48°, 51.77°, and 76.26° attributed to Ni substrate. It can be concluded that the pure phase perovskite structured BiFeO_3 can be obtained at 500 and 550°C with 10% bismuth overdoses, strong peaks characteristic of BiFeO_3 was obtained with a small amount of $\text{Bi}_{25}\text{FeO}_{40}$ and Bi_2O_3 . In addition, the main phase of the prepared sample was changed to $\text{Bi}_{25}\text{FeO}_{40}$ at 600°C.

3.2. Scanning electron microscopy: Since FTO is easily tailored to the shape for SEM measurement. The pre-experiment results show that there is no significant difference in the morphology of BiFeO_3 on Ni and FTO [17]. The SEM images of the film ($\text{Bi:Fe} = 1.10:1.00$) on the FTO substrate at different calcination temperatures are measured and displayed in Fig. 3. With the calcination temperature increased, the particles size becomes larger. As the calcination temperature increased from 450 to 550°C, the interface between the particles becomes clearer. This indicated the increase of crystallinity of the sample, which is in good agreement with the results of XRD. It can be seen in the SEM images that BiFeO_3 samples are well crystallised with the clearest interface and well-distributed size at 550°C. The biggest difference in particle size was observed in the sample at 600°C, but the grain interface is not clearer than 550°C. It is proposed that the change in particle size and distribution was the result of the phase change

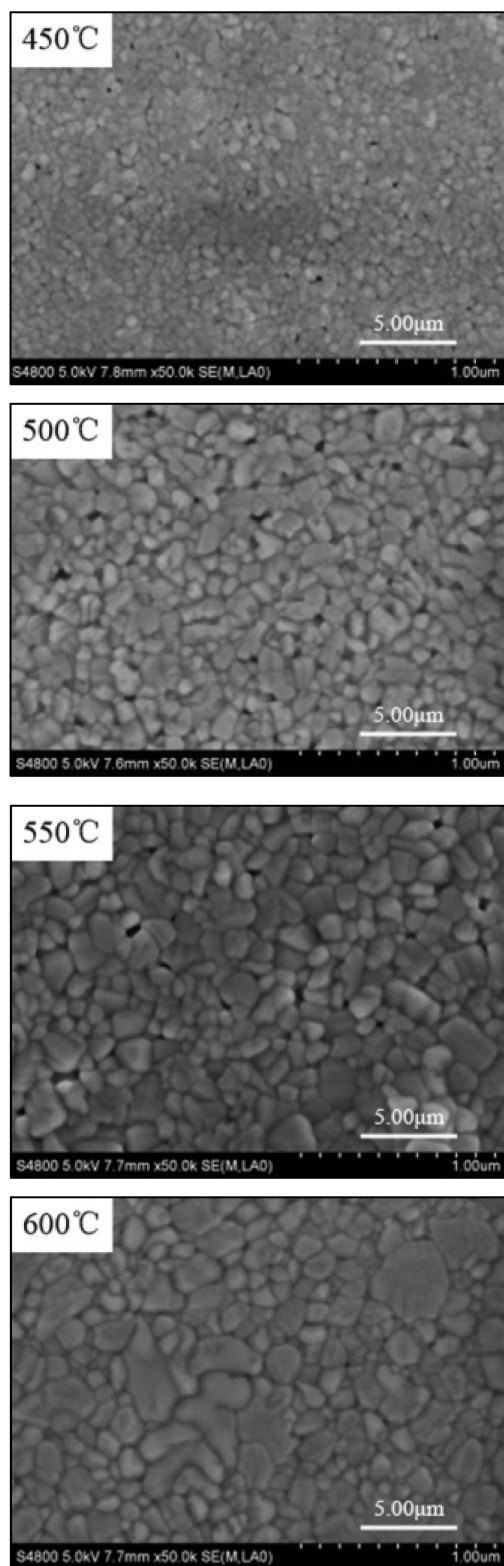


Fig. 3 SEM images of the prepared samples (Bi:Fe = 1.10:1.00) at different calcination temperatures

from BiFeO₃ to Bi₂₅FeO₄₀ at 600°C, this is also supported by the results of XRD. Also, we speculated that the grain interface at 600°C is less clear than that at 550°C because of the formation of the new crystal phase of Bi₂₅FeO₄₀.

3.3. UV–Vis spectroscopy: Fig. 4 shows the UV–Vis diffuse reflectance absorption spectra of the film (Bi:Fe = 1.10:1.00) on Ni

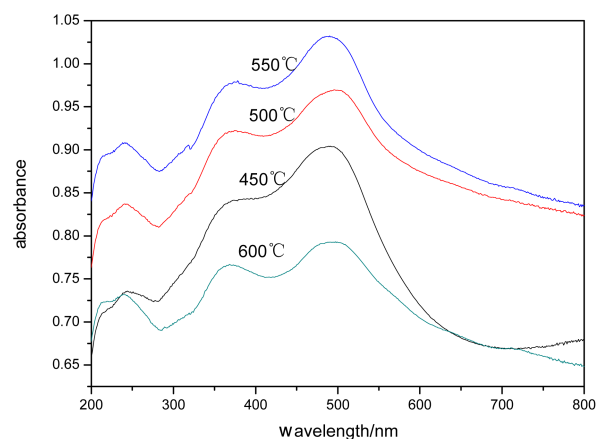
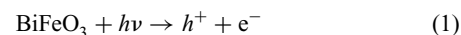


Fig. 4 UV–Vis diffuse reflectance spectra of the prepared samples (Bi:Fe = 1.10:1.00) at different calcination temperatures

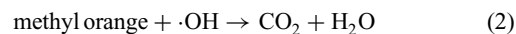
substrate at different calcination temperatures. As can be seen from Fig. 4, compared with the absorption in the UV region, all samples showed stronger absorption in the visible light region. This is consistent with the fact that BiFeO₃ nanoparticle, as a photocatalyst, is capable of responding to visible light [18–20]. Different absorption peaks appeared in samples, combined with the existence of different phases as shown in XRD. It is known that bismuth oxide has a band gap of 2.7–2.9 eV while compound oxides of bismuth and iron have a band gap of 2.0–2.2 eV. With the calcination temperature increased, absorbance intensity in both UV and visible regions enhanced. The strongest absorbance intensity of the sample was obtained at 550°C. Well crystallised and well distributed particle size of BiFeO₃ sample was obtained at 550°C, which made the BiFeO₃ sample had a larger surface area and thus then it is beneficial to the absorption of light.

3.4. Effect of resourceful treatment of salty organic wastewater: The resourceful treatment process of salty organic wastewater is the coupling of hydrogen preparation by electrolysis water, oxidation degradation of methyl orange by electrocatalysis, hydrogen preparation and oxidation degradation of methyl orange by photocatalysis. With the hydrogen evolution on the cathode, the concentration of OH[−] increases. Cd(OH)₂ was precipitated. The resourceful treatment process of salty organic wastewater can be described as follows:

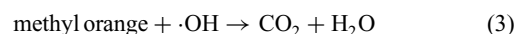
On anode
light excitation



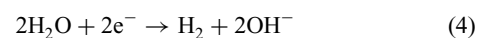
photocatalytic oxidation



electro-catalytic oxidation



On cathode
hydrogen revolution



In electrolyte solution near the cathode

removal of Cd²⁺



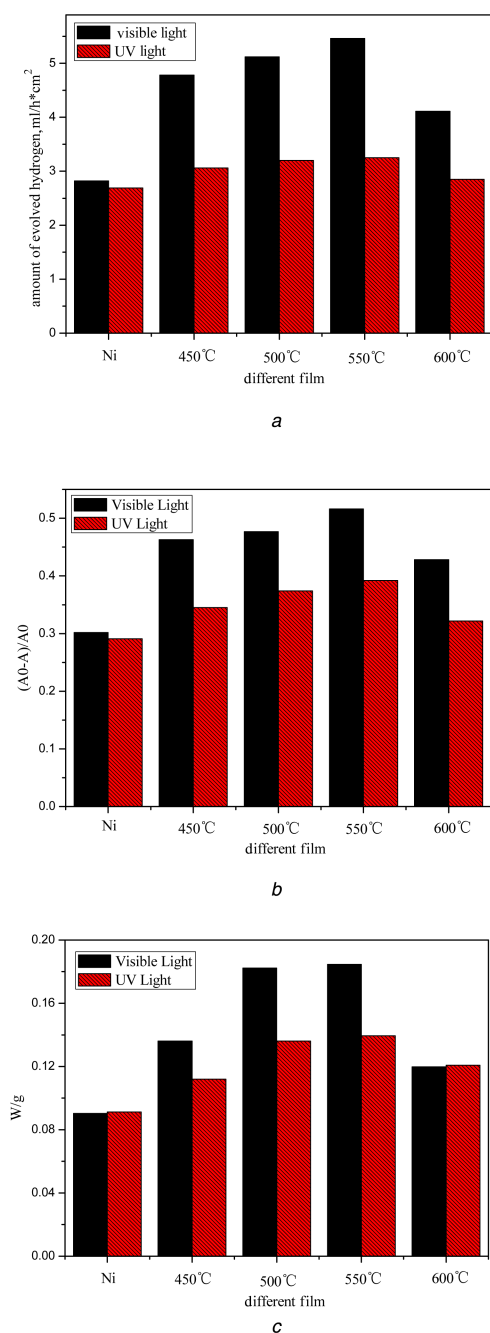


Fig. 5 Results of treatment of model wastewater with BiFeO₃/Ni anodes at different calcination temperatures
a Hydrogen preparation efficiencies
b Degradation of methyl orange
c Precipitation weight of calcium hydroxide

The symbols $h\nu$, h^+ and e^- express photo, photohole, and photo-electron, respectively. The hydroxyl radical $\cdot\text{OH}$ is a typical representative of the active oxygen species with strong oxidative activity. The resourceful treatment of salty organic wastewater assisted by photo-electric-catalyst (Bi:Fe = 1.10:1.00) samples of different calcination temperature was evaluated using a device mentioned in Fig. 1. The comparison of the results of resourceful treatment of the wastewater was shown in Fig. 5 using pure Ni foil and Ni foil modified by BiFeO₃ samples under different calcination temperatures as anodes. The H₂-production (Fig. 5a), the degradation rate of methyl orange (Fig. 5b) and precipitation weight of cadmium hydroxide (Fig. 5c) under visible light irradiation and UV irradiation were displayed, respectively.

The results of H₂ production, the degradation rate of methyl orange and precipitation weight of cadmium hydroxide with Ni foil modified by all oxide samples are much better than pure Ni foil. With the same voltage (2.0 V), UV and visible light irradiation, the highest H₂-production rate (5.46 ml/h·cm² with Vis, 3.25 ml/h·cm² with UV), methyl orange degradation rate (51.6% with Vis, 39.2% with UV) and the precipitation weight of cadmium hydroxide (0.1846 g with Vis, 0.1394 g with UV) were obtained with Ni foil modified by the film (Bi:Fe = 1.10:1.00) calcined at 550°C. The reasons for the high photo-electro-catalytic activity on the Ni anode modified by the film calcined at 550°C for the resourceful treatment of the wastewater are as follows: (i) there were a larger surface area and catalytic active site on the anode surface obtained at 550°C because of its small and well distributed particle size of BiFeO₃ film. (ii) The strong absorbance intensity of BiFeO₃ sample was obtained at 550°C and more electrons and holes were generated after the photo-excitation. (iii) There was more and high crystallinity BiFeO₃ phase obtained at 550°C and BiFeO₃ phase has high photo-electro-catalytic activity.

4. Conclusions

(1) The Ni foil modified by the film with a different atomic ratio of Bi to Fe was prepared by the method of spin coating-calcination at different temperatures. At 550°C, calcination with Bi:Fe = 1.10:1.00, BiFeO₃ films are well crystallised with clear interface and well distributed small particle size having the highest light absorption intensity.

(2) The photo-electro-catalytic process of the resourceful treatment of salty organic wastewater was suggested and experimentally achieved using the Ni anode modified by the BiFeO₃ film and with the UV/Vis irradiation on the anode. The degradation of organic pollutants, recovery of heavy metal ions, and hydrogen production take place at the same time in the process. The excellent photo-electro-catalytic activity was exhibited with the Ni anode modified by BiFeO₃ film at 550°C calcination with Bi:Fe = 1.10:1.00.

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6 References

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