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Cu-doped flower-like hematite nanostructures for efficient water splitting applications

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ABSTRACT

This study reports the successful preparation of Cu-doped hematite (α-Fe_2O_3) flower-like nanostructures with different Cu concentrations on FTO glass substrates using a facile hydrothermal method. The Cu-doped α-Fe_2O_3 flower-like nanostructure combines the advantage of p-type doping with the feature of a flower-like architecture. The prepared nanostructure film was applied as a photocathode in a photoelectrochemical (PEC) water splitting experiment and achieved a significantly improved photocurrent density of -5.34 mA cm^{-2} at -0.6 V vs. reversible hydrogen electrode (RHE) for 1 mol% Cu doping. The obtained photocurrent is about 4.85 times higher than that of the pure α-Fe_2O_3 based photoelectrode. The incorporation of Cu into α-Fe_2O_3 results in a dramatic enhancement in the water splitting performance. The enhancement is gained through an improvement in light harvesting and charge carrier separation. The copper-modified α-Fe_2O_3 sample also exhibited an up shift in the conduction band edge potential, which is energetically favorable for the water reduction reaction. This result demonstrated high performance PEC water splitting as a potential route for the production of hydrogen gas using a single Cu-doped α-Fe_2O_3 photoelectrode without the need for other catalysts and hybrid structures.

1. Introduction

Semiconductor assisted photoelectrochemical (PEC) water splitting has attracted considerable interest for the mass production of hydrogen (H_2) gas as a clean fuel source [1–3]. PEC water splitting is a simple and low cost process because it only requires abundant resources, such as a semiconductor electrode, water and light. Semiconductors with the appropriate band gap; high light absorption capacity and good majority carrier conductivity are favorable for carrying out the water splitting reaction. However, finding a stable semiconductor under acidic and alkaline electrolyte solution; with maximized solar light absorption and sufficient energy to drive water splitting has been a long-standing research challenge. In this regard, hematite (α-Fe_2O_3) is used widely as semiconductor photoelectrode of PEC cells due to its ability to absorb substantial amounts of incident light (band gap, 2–2.2 eV), chemical stability (pH >3), low cost and abundance in nature [4,5]. On the other hand, the application of α-Fe_2O_3 as a photoelectrode of PEC cells has been limited by its poor majority carrier conductivity and high recombination property (diffusion length <10 nm) [6]. In addition, the conduction band edge of α-Fe_2O_3 is below the H^+/H_2 redox potential, which hinders the spontaneous water reduction reaction under visible light radiation [7]. Several approaches have been implemented to improve the performance of hematite-based PEC water splitting. One of the most common practices has been the introduction of impurity ions into the α-Fe_2O_3 host via doping. Doping facilitates the separation of photo exited electrons and holes by improving conductivity [8,9]. Pure α-Fe_2O_3 is intrinsically an n-type semiconductor because of the presence of oxygen vacancies [10]. On the other hand, α-Fe_2O_3 can be converted easily to a p-type semiconductor by doping with the appropriate impurity ions, such as Mg^{2+}, Cu^{2+}, Zn^{2+}, and N [11–13]. P-type α-Fe_2O_3 generates a cathodic current and can be used as a photocathode in PEC cells to drive the water reduction reaction [14]. P-type doping not only increases the hole conductivity, but also modifies the band edge positions of semiconductors to satisfy the thermodynamic requirement for water splitting, which means both the conduction and valence band energy level need to straddle the redox potential of water [15]. In addition, p-type α-Fe_2O_3 is also used together with other n-type semiconductors as p–n junction type PEC cells, which provide an

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improved photovoltage to overcome the band gap mismatch problem between semiconductors and electrolyte [16–18]. Although p-type doping of α-Fe_2O_3 enhances the majority carrier and improves the PEC performance, its enhancement effect depends on the dopant concentration used. Therefore, the relationship between the doping concentration and PEC performance needs to be addressed.

An efficient photocathode architecture is another determining factor for the effective absorption of light and charge collection. In this regard, nanostructured photoelectrodes with one dimensional (1D) structures, such as nanotubes [19], nanorods [20,21], and nanowires [22,23], are favorable candidates due to their short carrier collection distance along the radial direction and the formation of an enlarged semiconductor liquid interface, which improves the photo generated current. Concerning 1D structure, Xiaopeng Qi et al. reported p-type, Zn-doped α-Fe_2O_3 nanotubes, which exhibited an improved cathodic current of approximately 40.4 μA cm^{-2} at 0.5 V vs. RHE. This improvement was gained through the adopted nanotube architecture and the enhancement in carrier concentration [24]. Hematite nano-flower structures are attractive three dimensional (3D) structures with a large surface area and porosity. Flower-like α-Fe_2O_3 nanostructures have been implemented for energy storage units and photo catalytic applications and have shown attractive performance [25,26]. On the other hand, to the best of the authors' knowledge, there are no reports of the application of p-type doped flower-like α-Fe_2O_3 nanostructures for applications to photo chemical water oxidation.

This paper reports the successful synthesis of p-type, Cu-doped hematite (α-Fe_2O_3:Cu^{2+}) flower-like nanostructures on FTO glass substrates using a facile hydrothermal technique. Different dopant concentrations of Cu ions were introduced to the α-Fe_2O_3 photoelectrode and their PEC water splitting performance was studied systematically. The prepared photoelectrodes generated a maximum current of −5.34 mA cm^{-2} at −0.6 V vs. RHE for 1 mol% Cu-doped hematite (α-Fe_2O_3: 1 mol% Cu^{2+}) photoelectrode. The resulting p-type α-Fe_2O_3:Cu^{2+} flower-like films were highly efficient for the electrochemical splitting of water and are promising candidates for the construction of p–n junction type PEC cells.

2. Experiments

2.1. Synthesis of cu-doped hematite flower-like nanostructures on FTO glass substrate

Analytical grade (Sigma Aldrich Co., Ltd.), $FeCl_3$ (97.0%), $CuSO_4$ (99.0%), $NaNO_3$ (99.0%) and HNO_3 (70.0%) were used as received without further purification. Hematite flower-like films were prepared using a hydrothermal method according to reported protocol [27]. Briefly, 0.015 mol of $FeCl_3$ and $CuSO_4$ were dissolved in a glass bottle containing 40 ml of water. Subsequently, 0.1 mol of $NaNO_3$ and 0.1 ml of HNO_3 were step by step added to the solution and stirred for 5 min. Next, FTO glass substrate was inserted to the solution and carefully placed at the bottom with conducting side facing upward. The sealed glass bottle was hydrothermally treated at 100 °C for 5 h. After the heat treatment hematite film was uniformly deposited on the surface of the FTO substrates.

Finally, the FTO glasses coated with the film were gently removed from solution, washed with deionized water, dried and annealed at 600 °C for 1 h to obtain the final flower-like hematite film.

Undoped and Cu-doped (0,0.5,1, 3 and 5 mol%) hematite photoelectrodes were prepared by mixing Fe and Cu precursors ($CuSO_4$ and $FeCl_3$) at 100:0, 99.5:0.5, 99:1, 97:3 and 95:5 mol ratios.

2.2. Characterization and measurement

The crystal structure of the synthesized samples was examined by X-ray diffraction (XRD) spectrometer (PANalyticalX'Pert PRO) with Cu Kα of 1.5406 Å. Morphology of the samples was studied by using Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi-S4700).

Absorption spectra of the samples were measured using a UV/vis spectrophotometer (V-630 model, Jasco Corporation) scanned between 200 and 800 nm.

The absorbance of each samples were carried out by using blank FTO glass as a base line. The PEC performance of the as prepared samples were investigated using a three-electrode electrochemical system under simulated AM 1.5 G solar light (100 mW cm^{-2}) illumination in 0.1 M NaOH solution (pH=12.6). In this system α-Fe_2O_3 flower-like film on FTO glass (active area, 2 cm × 1.5 cm) was used as a working electrode while Ag/AgCl and platinum wire were used as the reference and counter electrode, respectively. Linear sweep voltammetry and amperometric measurements were carried out in a two-electrode configuration system using α-Fe_2O_3 flower-like film on FTO substrate and platinum wire, as working and counter electrode, respectively. Mott–Schottky measurements were performed using electrochemical impedance analyzer; with AC amplitude of 10 mV and frequency range between 100 kHz and 0.1 Hz in a 0.1 M NaOH electrolyte solution. All measurements were performed with the same three-electrode configuration in the dark.

3. Result and discussion

Copper-doped α-Fe_2O_3 flower-like nanostructure film were synthesized on FTO glass substrates using a facile hydrothermal technique followed by sintering at 600 °C in air. After annealing, the film color changed from yellow to red, indicating the conversion from FeOOH to a α-Fe_2O_3 phase. Fig. 1a–d shows the FESEM images of the prepared samples. The image revealed a flower-like morphology consisting of a bunch of nanorods with the appearance of a flower. The nanorods had approximate diameter of 100 nm and length of 1.2 μm, firmly grown on FTO glass.

Fig. 1a shows a schematic diagram of the entire fabrication process. The absence of other structures at all doping concentrations could indicate the incorporation of the dopant ions into the α-Fe_2O_3 lattice or interstitial sites. On the other hand, further increases in the growth time and temperature will result in aggregation of the nanorods, leading to an oriented attachment to make a 3D flower-like nanostructure [26,28]. The flower-like morphology has a large surface area that enhances the interface surface area between α-Fe_2O_3 and water molecules, which is desirable for high performance water splitting.

Fig. 2 shows XRD patterns of the pure and Cu-doped flower-like α-Fe_2O_3 nanostructures sintered at 600 °C in air for 1 h. The plot shows similar peaks for all the samples which is readily indexed to the α-Fe_2O_3 nanostructures (JCPDS 33-0664) except for the peaks from the FTO glass. The XRD peak of FTO glass is also shown as a reference. The sharp peaks indicate good crystallinity and no peaks related to FeOOH were observed, confirming the complete conversion of the samples to a α-Fe_2O_3 phase. Two strong peaks at [110] and [104] were observed for both doped and pure samples, which are consistent with other report for nano-flower structure [29].

The elemental profile for doped samples was examined by EDX, as shown in Fig. 2b. The EDX data revealed the existence of Fe, O, and Cu with a relative concentration of 70.27, 26.51 and 3.22 wt%, respectively, corresponding to 5 mol% Cu doping. The EDX data for 0.5, 1 and 3 mol% Cu doping were not detectable due to small doping amounts.