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A flexible bio-inspired H_2-production photocatalyst

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ABSTRACT

Photocatalytic hydrogen generation from water splitting offers a viable potential solution for utilizing solar energy. Here we report a feasible synthesis of flexible bio-inspired $Zn_{0.5}Cd_{0.5}S$@PAN (polyacrylonitrile) mat-shaped photocatalyst with leaf-like structure, which shows high photocatalytic H_2-production activity with a rate of 475 μmol h^{-1} per 50 mg of the photocatalyst and an apparent quantum efficiency of 27.4% at 420 nm. The hierarchically porous structure of the mat-shaped $Zn_{0.5}Cd_{0.5}S$@PAN greatly enhances the molecular diffusion/transfer kinetics, and enlarges the utilization efficiency of light through the multiple reflections and scattering effect. Moreover, a good dispersion of $Zn_{0.5}Cd_{0.5}S$ nanoparticles (NPs) on the surface of PAN nanofibers prevents their aggregation. These features account for high H_2-production activity of $Zn_{0.5}Cd_{0.5}S$@PAN. Remarkably, the integrity and flexibility of $Zn_{0.5}Cd_{0.5}S$@PAN mat-shaped photocatalyst facilitate their separation and re-use after photocatalytic reaction. Hierarchically porous leaf-like mat-shaped photocatalysts with high photocatalytic activity and stability should also find potential applications in solar cells, catalysis, separation and purification processes.

1. Introduction

Since Fujishima and Honda reported photoelectrochemical water splitting in 1972 [1], the semiconductor-driven photocatalytic splitting of water has been considered as an ideal strategy to generate high-density and clean hydrogen energy from solar energy [2–8]. To date, however, the efficiency of water splitting on visible-light responsive photocatalysts is far from the requirement for practical applications [9–15]. Moreover, among known photocatalysts, the most efficient ones are usually nanopowders [16–25], the separation and recycle of which from reaction solution is another major technological obstacle for advancing their commercial applications. Accordingly, numerous attempts have been made toward development and large scale production of highly efficient and easily recyclable photocatalysts [26,27].

Recently, flexible energy-conversion systems have attracted a lot of attention due to their unique advantages, such as flexibility, shape integrity, light weight, repeatability and so on. They have been used in flexible lithium-ion batteries and flexible supercapacitors [28,29]. As reported, the flexible materials can withstand external forces, and keep the integrated shape after reaction. Thus, the use of flexible materials as photocatalysts could solve the recycling problem of nanopowder photocatalysts. Unfortunately, there are few flexible materials directly used as H_2-production photocatalysts.

As we know, the photosynthesis in nature (Fig. 1) mainly occurs on the chlorophylls immobilized on flexible skeletons of leaves, and the generated nutrients are transferred to the trunk through these skeletons. The flat and flexible shape of leaves can greatly increase the area available for light absorption and capture of reactants, and consequently, enhance the photosynthesis process. Moreover, the stomata in leaves are critical for diffusion and release of reactants and products (CO_2, H_2O and O_2). Inspired by nature, one could envision the immobilization of highly efficient nanoparticle photocatalysts on flexible substrates to construct leaf-like structured photocatalysts. However, weak interactions between substrate and photocatalyst nanoparticles can cause the stripping of photocatalysts, which seriously restrict their practical applications [30–33]. Polyacrylonitrile (PAN) nanofibers are very attractive polymers due to their flexibility, lightweight, chemical and light resistance. Though some semiconductor/PAN composite photocatalysts have been reported [34–36], the lack of intimate contact and uniform dispersion caused by the incompatibility between inorganic semiconductor and organic PAN led to the unsatisfied performance. In this study, we took advantage of the C≡N functional groups of PAN nanofibers and used them to capture metal cations from solutions via coordination-type interactions, which resulted in the uniform deposition of highly efficient photocatalyst nanoparticles on the surface of these nanofibers [37]. In addition, we utilized the propensity of PAN

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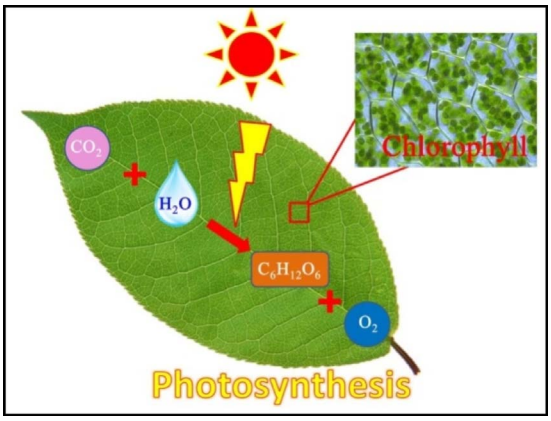

Fig. 1. The natural photosynthesis process occurring on leaves.

nanofibers to assembly into an integrated flexible mat through electrospinning. This mat has the same flat and flexible shape as a leaf, and features a hierarchically porous structure that can play a similar role as stomata in leaves. These special features make PAN mat a perfect flexible substrate candidate for constructing highly efficient leaf-like structured composite photocatalysts.

Herein, a flat and flexible PAN mat (PAN-Mat) is chosen as a substrate for immobilization of $Zn_xCd_{1-x}S$ solid solution photocatalyst nanoparticles. $Zn_{0.5}Cd_{0.5}S$ with sphalerite phase structure is the highly active solid solution nanosized photocatalyst for H_2-production as reported elsewhere [38,39]. The prepared leaf-like $Zn_{0.5}Cd_{0.5}S$@PAN composite mat (ZCS@PAN-Mat) has intriguing properties due to the structural advantages of PAN mat and excellent photocatalytic H_2-production activity of $Zn_{0.5}Cd_{0.5}S$ NPs (ZCS-NP). Moreover, during the deposition of metal sulfides, PAN can be further sulfurized into sulfurized-PAN, which results in better affinity toward surface deposition of sulfides. This process favors uniform deposition of metal sulfides NPs ($Zn_{0.5}Cd_{0.5}S$) on the PAN mat. As a result, this integrated flexible ZCS@PAN-Mat shows high photocatalytic hydrogen evolution activity, even higher than that of the pure ZCS-NP. Cycle stability tests indicate that the flat and flexible composite mat exhibits good structure stability during photocatalytic hydrogen generation. The ZCS@PAN-Mat can be easily re-used without obvious loss of photocatalytic activity.

2. Experimental details

2.1. Synthesis of flexible PAN nanofibers mat (PAN-Mat)

PAN nanofiber mats were prepared via electrospinning method. Firstly, 1 g of PAN powder was completely dissolved in 10 mL of *N*, *N*′-dimethylformamide (DMF) and then the obtained transparent light-yellow solution was filled into a 20 mL syringe with a 0.6 mm inner-diameter metal needle. The details of electrospinning parameters, applied high voltage, feeding rate of the solution and distance between the needle and collection plate, were set at 15 kV, 0.5 mL/h and 15 cm, respectively. After electrospinning for approximately 10 h, the white PAN flexible mat was peeled off from the collection plate and dried at 80 °C.

2.2. Synthesis of $Zn_{0.5}Cd_{0.5}S$@PAN flexible mat (ZCS@PAN-Mat)

In a typical synthesis of ZCS@PAN-Mat, 0.5 mmol of zinc acetate dihydrate, 0.5 mmol of cadmium acetate dihydrate and 2 mmol of thiourea were dissolved into 40 mL of ethanol to form a mixture solution, and then, a piece of integrated PAN-Mat (50 mg) was dipped into the above solution. After sonication for 10 min, the solution with PAN-Mat was transferred into a Teflon-lined stainless-steel autoclave with a total volume of 50 mL and kept at 120 °C for 12 h. After cooling down, the resulting yellow ZCS@PAN-Mat was washed with water and ethanol thoroughly, and then dried in oven at 80 °C. For the purpose of comparison, pure $Zn_{0.5}Cd_{0.5}S$ nanoparticles (ZCS-NP), CdS nanoparticles (CS-NP) and ZnS nanoparticles (ZS-NP) were also prepared by the same method just without PAN-Mat. The CdS@PAN flexible mat (CS@PAN-Mat) and ZnS@PAN flexible mat (ZS@PAN-Mat) were prepared using 1 mmol of cadmium acetate dihydrate or 1 mmol of zinc acetate dihydrate to replace 0.5 mmol of zinc acetate dihydrate and 0.5 mmol of cadmium acetate dihydrate. The SPAN-Mat was prepared without the addition of Zn and Cd precursors, the other steps were the same as that in the case of ZCS@PAN-Mat.

2.3. Photocatalytic hydrogen evolution experiment

The photocatalytic hydrogen evolution experiments were performed in a 200 mL cylindrical Pyrex flask with three openings sealed by silicone rubber septa. A 350 W Xe lamp was used as light source to trigger the photocatalytic reaction. A filter was positioned between the light source and reactor to cut off UV light ($\leq$420 nm). The distance between light source and reactor was set as 15 cm. In a typical photocatalytic reaction, a piece of prepared ZCS@PAN-Mat (50 mg) was soaked in 80 mL of mixture solution containing Na_2S (0.35 M) and Na_2SO_3 (0.25 M). Bubbled with N_2 for 20 min, the flask was sealed and irradiated using visible light for several hours. The generated H_2 gas was analyzed by a Shimadzu GC-14C gas chromatograph with TCD detector for every hour. The apparent quantum efficiency (QE) of photocatalytic reaction was measured using the same reaction conditions except that the light source was four LEDs with 420 nm wavelength. The distance between these LEDs and reactor was set as 1 cm. At this distance, the light intensity of each LED was measured to be 6.0 mW cm^{-2}. The irradiation area on the reactor for each LED was about 1 cm^2. The QE was calculated by using the following Eq. (1):

$$QE[\%] = \frac{\text{numberofreacted electrons}}{\text{numberofincidentphotons}} * 100\% = \frac{\text{number ofevolved}H_2 \text{ molecules} * 2}{\text{number ofincidentphotons}} * 100\% \quad (1)$$

2.4. Electrochemical impedance spectra (EIS) measurements

EIS measurements were performed on an electrochemical analyzer (CHI660C Instruments) equipped with a standard three-electrode system. A Pt wire acted as the counter electrode, the Ag/AgCl (saturated KCl) as the reference electrode, and the FTO glass coated by the sample as the working electrode. The sample area on the FTO glass was about 1.5 cm^2. A UV-LED (3 W, 365 nm, Shenzhen LAMPLIC Science Co. Ltd., China) was used as light source and 0.5 M Na_2SO_4 was used as the electrolyte. The electrochemical impedance spectra (EIS) were recorded over a frequency range of 1–10^5 Hz with an amplitude of 5 mV at 0.5 V.

2.5. Characterization

The X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max-RB X-ray diffractometer (Japan) with Cu *Kα* radiation at a scan rate (2*θ*) of 0.05° s^{-1}. A field emission scanning electron microscope (FESEM, JEOL 7500F, Japan) and a high-resolution transmission electron microscopy (TEM, JEOL 2100, Japan) were employed for the morphology and microstructure observations. Nitrogen adsorption and desorption isotherms were measured using a gas adsorption analyzer (Micromeritics ASAP 2020, USA). The pore size distribution curves were obtained by the Barret–Joyner–Halender (BJH) method using adsorption branches of adsorption-desorption isotherms. The light absorbance performance of the samples was investigated on a Shimadzu UV-2600 UV–vis spectrophotometer (Japan). The chemical composition of the samples and the chemical states of elements were characterized