



Construction of Molybdenum Disulfide/Biological Structure Carbon Composite Photocatalysts and Their Photocatalytic Hydrogen Production

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Wang S, Ding J, Wang C, Li W, Chen Z, Liu C and Chen F (2022) Construction of Molybdenum Disulfide/Biological Structure Carbon Composite Photocatalysts and Their Photocatalytic Hydrogen Production. Front. Mater. 9:889499. doi: 10.3389/fmats.2022.889499 The hydrothermal calcination method using bamboo leaves as the biological template, thiourea as the sulfur source, and molybdenum chloride as the molybdenum source was employed to synthesize the molybdenum disulfide/biological structure carbon (MoS₂/C) photocatalytic composites with different concentrations of molybdenum chloride. The thermal decomposition behavior, surface morphology, phase structure, BET specific surface area, optical and photoluminescence properties, and photocatalytic activity of MoS₂/C photocatalytic composites with different concentrations of molybdenum chloride were studied. The results showed that the optimal temperature for synthesizing MoS₂/C photocatalytic composites is 700°C. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations show that the hydrothermal calcination method can be used to load MoS₂ onto the biological carbon and form a structurally stable composite system. Analysis of optical and photoluminescence properties shows that the MoS₂/C composites prepared by the hydrothermal calcination method with the concentration of molybdenum chloride of 0.20 mol/L exhibit a high charge transfer and separation efficiency. Photocatalytic experiments show that the MoS₂/C composites prepared by the hydrothermal calcination method with the concentration of molybdenum chloride of 0.20 mol/L have a high photocatalytic activity and cyclic stability. This excellent synthesis strategy can be used to synthesize other photocatalytic hydrogen production materials.

Keywords: hydrothermal calcination method, molybdenum disulfide, biological structure carbon, photoluminescence properties, photocatalytic activity

INTRODUCTION

With the development of world economy, non-renewable resources are gradually exhausted, so it is necessary to develop renewable resources to meet the needs of human life (Gouma et al., 2016; Wang et al., 2021a; Wang et al., 2021b; Cheng et al., 2021; Jia et al., 2021; Li et al., 2021; Zhang et al., 2021). Photocatalytic hydrogen production is an effective technology for the utilization of renewable resources and has attracted extensive attention from researchers all over the world (Kais et al., 2019; Luo et al., 2019; Ravishankar et al., 2019; Chen et al., 2019; Wang et al., 2020a). Molybdenum

1

disulfide (MoS₂) is a potential photocatalyst for photocatalytic decomposition of water to produce hydrogen, which has been applied in this field (Zhang et al., 2019). MoS₂ is the main component of molybdenite in nature. Block MoS₂ is made up of a large number of single or small layers of MoS₂ combined with interlayer van der Waals force and stacked. According to the different stacking modes and layers in the crystal, layered MoS₂ can be divided into three types, namely, 1T, 2H, and 3R, where the number represents the layers of the unit cell MoS₂; T, H, and R are trigonal, hexagonal, and rhombohedral, respectively (Zhang et al., 2018). 1T-MoS₂ and 3R-MoS₂ are metastable, while 2H-MoS₂ is stable and exhibits excellent semiconductor properties (Sarno and Ponticorvo, 2019).

Single or small layer MoS₂ material is a direct band gap semiconductor; its band gap width is 1.82 eV, so it can produce optical response to the visible light in the sunlight (Rumyantsev et al., 2007). However, it is easy to form folds and clusters due to the high surface activity of MoS2 material, which greatly reduces the surface area of MoS2 semiconductors and increases the composite probability of the photogenerated electron-hole pair. In addition, there is a significant photocorrosion effect in MoS2 semiconductors, which limits the further improvement of photocatalytic semiconductor materials. To solve these problems, researchers put forward a variety of solutions. Yuan et al. (Qi et al., 2019) prepared MoS₂/ reduced graphene oxide (rGO) composite catalytic material, whose excellent photocatalytic performance can be attributed to graphene acting as an electron transfer bridge to improve the transfer of charge carriers. Li et al. (2014) conjugated MoS₂ nanosheets to (graphite phase carbon nitride) g-C₃N₄ through an easy ultrasonic chemical method to form the MoS₂/C₃N₄ heterostructure. In this structure, MoS₂ is used as an electron trap to prolong the life of the separated electron-hole pair and can be used for the photodegradation of organic dyes. Meng and his team (Meng et al., 2013) deposited 5-20 nm p-type MoS₂ nanosheets on n-type nitrogen-doped reduced graphene oxide (N-rGO) nanosheets to form multiple p-n junctions on each rGO nanosheet. The p-MOS₂/N-rGO heterostructure greatly enhanced charge generation and inhibited recombination and showed high photocatalytic activity for hydrogen evolution reaction in the wavelength range from ultraviolet to near-infrared light. Generally, bamboo leaves are used as a biological template to prepare semiconductor oxide materials with a special structure, which can enhance the physical and chemical properties of the semiconductor oxide materials (Li et al., 2007; Wang et al., 2018). It is of great significance to develop a new synthesis route using bamboo leaves as biological templates to prepare MoS₂ and enhance its charge-carrier migration and separation efficiency.

In this study, we proposed to use bamboo leaves as biological templates to prepare biostructured carbon and to prepare MoS₂/biological structure carbon (C) composites with four concentration gradients by the hydrothermal calcination method. The thermal decomposition behavior, surface morphology, phase structure, BET specific surface area, optical and photoluminescence properties, and photocatalytic activity of MoS₂/C composites with different concentrations of

molybdenum chloride were comparatively studied by using various instruments. Simultaneously, the cyclic stability experiment of photocatalytic hydrogen production was performed. The MoS_2/C composites prepared by the hydrothermal calcination method with the concentration of molybdenum chloride of 0.20 mol/L exhibit lowest emission intensity, high charge transfer, and separation efficiency, as well as high photocatalytic activity.

MATERIALS AND METHODS

Preparation of MoS₂/C Composite Photocatalysts

Thiourea and molybdenum chloride, with the molar ratio of 1:1, were accurately weighed. Four solutions with different concentrations of molybdenum chloride with 0.05, 0.10, 0.15, and 0.20 mol/L were prepared. The bamboo leaves are pretreated in a tubular furnace under a nitrogen atmosphere at a sintering temperature of 800°C. Four 20 g pretreated bamboo leaf biological templates were weighed and completely immersed in the aforementioned solution. After immersing for 24 h, the templates were transferred to the reaction kettle with teflon lining. The reactor was transferred to a drying oven and held at 160°C for 6 h to obtain four concentrations of precursors. The precursors were transferred to quartz tubes in a tubular furnace, MoS₂/C composite photocatalysts obtained by heating the precursors from room temperature to 800°C at a rate of 5°C/min under the exposure of nitrogen protection gas.

Material Characterization

The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) of precursors were characterized by using the SDT Q600 simultaneous thermal analyzer (TA instruments, Inc. United States) under the exposure of nitrogen protection gas. The heating rate, the air flow rate, the injection volume, and the temperature range are 20 K/min, 100 ml/min, 2 mg, and 25-800°C, respectively. The microstructures of the MoS₂/C composite photocatalysts were observed by scanning electron microscopy, while the fibers and particles constituting membranes were characterized by using an Apollo 300 scanning electron microscope (SEM) and Libra 200 type transmission electron microscope (TEM) produced by Carl Zeiss IRTS, Germany. The MoS₂/C composite photocatalysts were characterized by using a Brook D8 Advance X-Ray diffractometer with the scanning angle of 20-80°, the scanning step length of 0.02° , and using Cu target K α ($\lambda = 0.154056$ nm) radiation with the working voltage of 40 kV and current of 40 mA. UV-visible absorption spectra of the MoS₂/C composite photocatalysts were measured by using an ultraviolet and visible spectrophotometer. The fluorescence spectra of the MoS₂/C composite photocatalysts were collected in a confocal Raman system using a He-Cd laser with the RGB laser system (325 nm, NovaPro 30 mW, Germany) at room temperature. Nitrogen adsorption experiments are performed through nitrogen adsorption equipment.

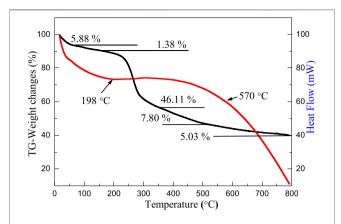


FIGURE 1 | TG–DSC curves of precursors of MoS $_2$ /C composites with the concentrations of molybdenum chloride of 0.20 mol/L prepared by the hydrothermal calcination method.

Photocatalytic Experiments

In order to investigate the photocatalytic properties of the prepared MoS₂/C composite photocatalysts, they were applied to the reaction of photocatalytic degradation of water to produce hydrogen and compared with the pure MoS₂. The Labsolar H₂ photolysis system was developed by Beijing Perfectlight Technology Co., Ltd., and the detection device was a Shanghai Tianmei GC7900 gas chromatograph produced by Shandong Jinpu Analytical Instrument Co. Ltd., with a Microsolar 300 high-performance analog daylight xenon lamp which was used as the simulation light source. For the experiment, 100 mg sample was added to 100 ml deionized water, and sodium sulfite was added as the sacrificial agent to carry out photocatalytic hydrogen production. The hydrogen production of each material was compared after 6 h of illumination.

RESULTS AND DISCUSSION

TG-DSC Analysis

Figure 1 shows the thermogravimetry (TG) and differential scanning thermal curves (DSC) of the precursor of MoS₂/C composites with the concentrations of molybdenum chloride of 0.20 mol/L prepared by the hydrothermal calcination method. The weight loss process of the precursor is divided into five stages. As the samples were dried at 40°C, the content of free water in the precursor was slightly lower, and the weight loss ratio of free water precipitation to evaporation was 5.88% (Artiaga et al., 2005; Hsu and Lin, 2009). Hydrothermal and drying processes can effectively reduce the free water content of the precursor, and the weight loss is only 1.38% in the heating range of 100-198°C, and the release and heat dissipation of free water and bound water are energy dissipation reactions, corresponding to an obvious endothermic process on the energy curve (Saldo et al., 2002; Tahmasebi et al., 2014). The third weightless stage mainly occurs in the range of 200-400°C, which is the main concentrated range of slow thermal decomposition of cellulose (Szcześniak et al., 2008; Kristanto

et al., 2021). A large number of groups in cellulose accompanied the pyrolysis decomposition, by recombination of functional groups of lignin, and the biological structure carbon begins to generate in large quantities (Mikheeva et al., 2021). After 400°C, a small amount of cellulose cleaves to produce small molecules, the groups continue to decompose, carbon elements rearrange, and hemicellulose enters the carbonization stage and undergoes strong decomposition until 450°C basically ends (Yadav et al., 2021; Zhao et al., 2021). The main reason of 7.80% weight loss was the fracture of old bonds and the formation of new bonds in lignin. At the final weightlessness stage of the precursor, cellulose completes the carbonization reaction, and the benzene ring in lignin is first unchained and then aromatized, forming an amorphous carbon biological structure (Krueger et al., 2021; Xia et al., 2021). The hemicellulose eventually forms the biological carbon (Kabachkov et al., 2020). In addition, during the heating process of 200-570°C, the energy curve of the precursor does not decrease significantly with the pyrolysis and carbonization rearrangement of organic matter but is in dynamic equilibrium. The phenomenon can be ascribed to the release of energy, and organic carbon absorption energy of the grain growth is roughly the same, so the energy changes in a dynamic balance. Based on the analysis of weight loss in the thermal decomposition stages mentioned previously, the weight stabilizes at 800°C.

Scanning Electron Microscopy Analysis

Figures 2A-H shows the SEM images of MoS₂/C composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L at different magnifications. At low magnification, the organic matter in the leaves could be transformed into biological carbon, and the microscopic morphology of the original template was completely preserved. The composite system is based on biological structure carbon, and MoS₂ particles are loaded on the thin layer of carbon. The obtained biological structure carbon material has two main functions: First, it can provide support for the loading of MoS₂ particles so that the material can resist the deformation caused by clusters or Oswald curing during high temperature calcination and avoid the collapse phenomenon. Second, a firm bond is formed between biological carbon and MoS₂ under the action of high temperature, and the photogenerated electrons in the semiconductor are transferred to the surface of biological carbon for the reduction reaction, reducing the possibility photogenerated electron-hole recombination. After the calcination process, a cluster phenomenon of MoS₂ nanoparticles was formed by the hydrothermal process under thermal action and presented a spherical structure; the diameter of spherical particles is about 2-5 µm. As the concentration of the sulfur source and molybdenum source increases in the hydrothermal process, the number of MoS₂ nanoparticles increases successively, and the cluster size increases with the concentration change. According to SEM observation, it can be inferred that the complex system has a high photocatalytic performance when

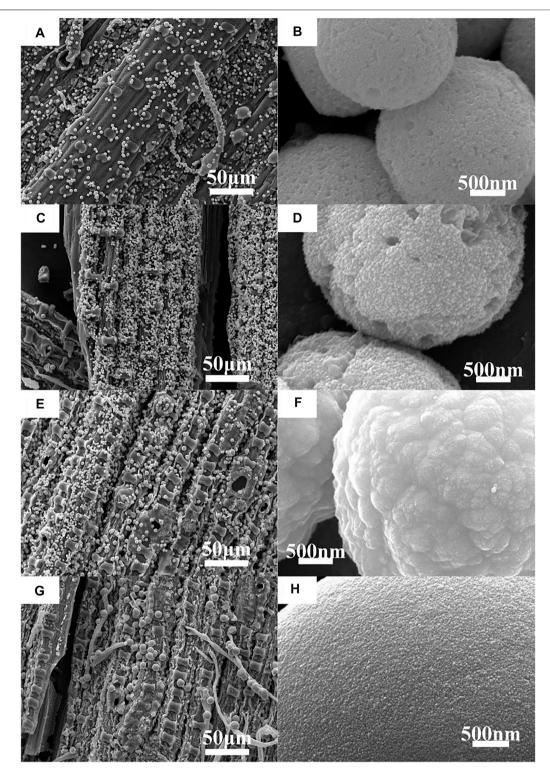


FIGURE 2 | SEM images and enlarged SEM images of MoS $_2$ /C composites with the different concentrations of molybdenum chloride prepared by the hydrothermal calcination method. (A,B) 0.05 mol/L, (C,D) 0.10 mol/L, (E,F) 0.15 mol/L, and (G,H) 0.20 mol/L.

the molybdenum chloride concentration is $0.2\,\mathrm{mol/L}$. This conclusion needs to be proven by photocatalytic experiments.

Transmission Electron Microscopy Analysis Figure 3 shows the TEM and HRTEM images of MoS_2/C composites prepared by the hydrothermal calcination method

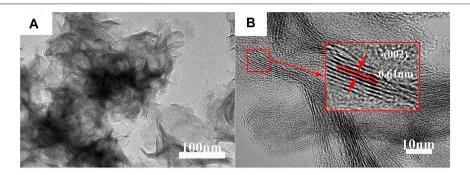


FIGURE 3 | (A) TEM and (B) HRTEM images of MoS₂/C composites prepared by the hydrothermal calcination method with the concentrations of molybdenum chloride of 0.20 mol/L.

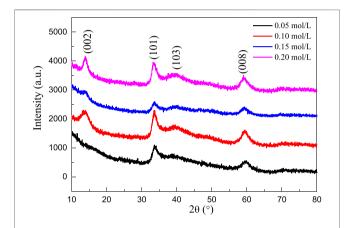


FIGURE 4 | XRD patterns of MoS₂/C composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L.

with the concentrations of molybdenum chloride of 0.20 mol/L. As can be seen from Figure 3A, a large number of MoS₂ nanoparticles are loaded on the a thin layer of the biological structure of carbon, indicating that the MoS₂ nanoparticles form clusters and undergo accumulation when loaded on the surface of carbon material, which is consistent with the SEM observation. Figure 3B was obtained by magnifying the edge of the TEM image by 10 times. From the figure, it can be found that the MoS₂ particles forming clusters are nanoscale with a particle size of about 15 nm. The crystal lattice fringe of the particles is obvious. TEM professional software is used to calculate the spacing of exposed crystal planes in the figure, and the value is 0.61 nm, corresponding to the (002) crystal plane of MoS_2 in the β -phase. Similarly, the biological structure of carbon obtained by this method is layered carbon, which further proves that hightemperature calcination is more beneficial to enhance the crystallinity of the layered carbon.

XRD Analysis

Figure 4 shows the XRD patterns of MoS₂/C composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including

0.05, 0.10, 0.15, and 0.20 mol/L. A series of characteristic peaks were observed at similar locations for the four products with different concentrations, and they all corresponded to the (002), (101), (103), and (008) crystal planes of β phase MoS $_2$ (JCPDS card no. 41-1049) at $2\theta=13.92,\,33.43,\,39.77,\,$ and $59.25^{\circ},\,$ respectively. In addition, there were no redundant miscellaneous peaks in the pattern, indicating that the prepared MoS $_2$ nanocrystal is of high purity. The crystallinity of the material increases with the increase in the concentration, and the crystal plane with the sharpest diffraction intensity is (101). The halfpeak width of the main characteristic peak of the material is wide, indicating that the average coherent scattering size of the material is small, and the concentration has no significant effect on the coherent scattering size of the material.

Optical Properties

Figure 5A shows the UV-Vis absorption spectra of molybdenum disulfide/biological structure carbon composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L. For the products obtained by the hydrothermal calcination method, the composite system absorbs all the light sources of the whole band because the color of MoS2 is black, and the material absorbs all the light sources of the whole band. However, the composite system absorbs the infrared light source but does not respond due to the limitation of the band gap. The concentration had no significant effect on the UV-Vis absorption capacity of the composite system. The band gap energy (Eg) values of molybdenum disulfide/biological structure carbon composites were prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L obtained by the UV-Vis absorption spectra using the Tauc relation (Gao et al., 2018; Gao H. J. et al., 2021; Wang et al., 2021c; Wang et al., 2022) from Figure 5B.

$$(F(R)h\nu)^n = A(h\nu - E_g), \tag{1}$$

where v, A, and n are the frequency, the absorption coefficient, and 2, respectively. The E_g values of molybdenum disulfide/

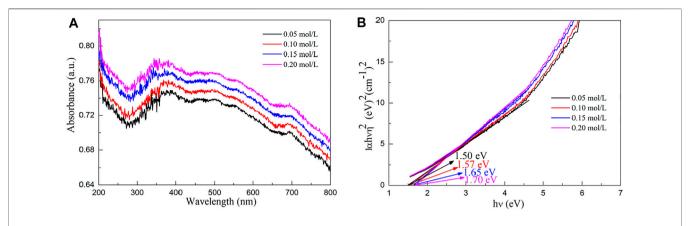


FIGURE 5 | (A) UV-Vis absorption spectra and (B) Eg values of molybdenum disulfide/biological structure carbon composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L.

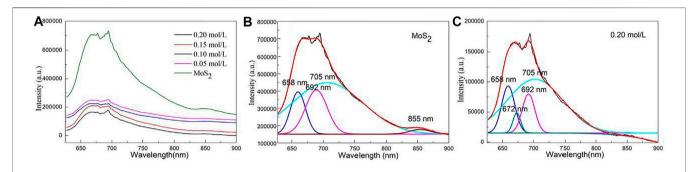


FIGURE 6 | (A) Emission spectra of MoS_2/C composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0, 0.05, 0.10, 0.15, and 0.20 mol/L. **(B)** Emission spectrum of pure MoS_2 could be resolved into three Gaussian peaks with the maxima at 658, 692, 705, and 855 nm. **(C)** Emission spectrum of MoS_2/C composites with the concentration of molybdenum chloride of 0.20 mol/L could be resolved into four Gaussian peaks with the maxima at 658, 672, 692, and 705 nm.

biological structure carbon composites prepared by the hydrothermal calcination method with the concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L are obtained by a simple intercept method. The Eg values of molybdenum disulfide/biological structure carbon composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/ L are 1.50, 1.57, 1.65, and 1.70 eV, respectively. The Eg value of molybdenum disulfide/biological structure carbon composites increases with the increasing molybdenum chlorate content. The Eg value of molybdenum disulfide/biological structure carbon composites decreases slightly than that of pure monolayer MoS₂ (1.80 eV). These results suggest that the molybdenum disulfide/biological structure carbon composites can respond to visible light.

Photoluminescence Properties

Figure 6A shows the emission spectra of MoS₂/C composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0,

 $0.05,\,0.10,\,0.15,\,{\rm and}\,0.20\,{\rm mol/L}.$ The emission peak of pure MoS_2 is mainly concentrated in the range of 575–900 nm and has the highest emission peak intensity compared with other samples. The intensity of emission peak decreases with the increase in the molybdenum chloride content. The MoS_2/C composites prepared by the hydrothermal calcination method with the concentrations of molybdenum chloride of 0.20 mol/L have the lowest emission intensity indicating that the sample exhibits the highest charge transfer and separation efficiency. Its high charge transfer and separation efficiency result in high photocatalytic activity for splitting water to produce hydrogen.

Figure 6B shows the emission spectrum of pure MoS₂ that could be resolved into three Gaussian peaks with the maxima at 658, 692, 705, and 855 nm. The peaks at 658 and 692 nm can be ascribed to the intrinsic luminescence peak of MoS₂, which is mainly composed of the photon energy radiated by the recombination of photogenerated electron-hole pairs in the MoS₂ semiconductor. The peaks at 705 and 855 nm can be assigned to the defect luminescence peak, which is mainly composed of fluorescence radiation generated by the sulfur lattice vacancy capturing electrons in the MoS₂ semiconductor

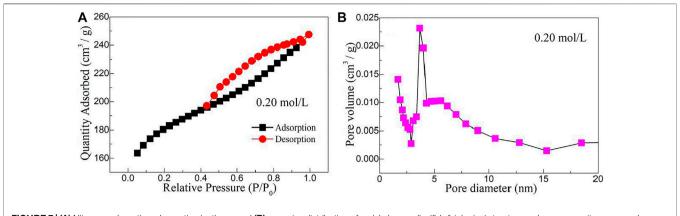


FIGURE 7 | (A) Nitrogen adsorption-desorption isotherm and (B) pore size distribution of molybdenum disulfide/biological structure carbon composites prepared by the hydrothermal calcination method with the concentration of molybdenum chloride of 0.20 mol/L.

and then recombination with photogenerated holes (Tang et al., 2020; Wang et al., 2020b; Wang and Tian, 2020; Gao H. et al., 2021; Wang S. F. et al., 2021).

Figure 6C shows the emission spectrum of MoS₂/C composites with the concentration of molybdenum chloride of 0.05 mol/L could be resolved into four Gaussian peaks with the maxima at 658, 672, 692, and 705 nm. This result differs from MoS₂ in two ways: one new peak at 672 nm can be observed, and the fluorescence emission peak at 855 nm is quenched. The peak at 672 nm can be ascribed to the interface defect formed by MoS₂ coupling with biological structure carbon particles. The quenching of the fluorescence emission peak at 855 nm may be due to the formation of MoS₂/C heterojunction which greatly enhances the separation and transportation of photogenerated carriers (Zhao et al., 2020; Chi et al., 2021). The intensity of the luminescent peak decreases with the increase in the content of molybdenum chloride. Generally, the charge carrier transfer and separation efficiency decrease with the increase in the luminescence intensity. The MoS₂/C composites with the concentrations of molybdenum chloride of 0.20 mol/L exhibit lowest emission intensity. Therefore, the results confirm that the MoS₂/C composites prepared by hydrothermal calcination method with the concentrations of molybdenum chloride of 0.20 mol/L have the highest charge transfer and separation efficiency.

Adsorption-Desorption Isotherm and Pore Size Distribution

Figure 7A shows the nitrogen adsorption–desorption isotherm of molybdenum disulfide/biological structure carbon composites prepared by the hydrothermal calcination method with the concentration of molybdenum chloride of 0.20 mol/L. Combined with the IUPAC classification method, the nitrogen adsorption–desorption isotherms belong to a typical type IV. When the relative pressure is at a low pressure (0–0.1), monolayer adsorption is carried out, and the adsorption capacity of the system increases gently. When the relative pressure is in the middle range (0.1–0.4), multilayer adsorption takes place, and

nitrogen molecules are adsorbed on the interlayer channels of the biological structure of carbon and the slit mesopores formed by the folds of MoS₂ nanosheets. Under the relative high pressure (0.4-1.0), capillary condensation is mainly carried out in the system, and the adsorption-desorption saturation equilibrium is achieved at a p/p0 of 1.0. The H₃-type hysteresis ring formed under high pressure indicates that there are a lot of slit pore mesoporous structures formed by the accumulation of sheet MoS₂ and biological structure carbon layer in the system. Combined with the related literature studies, the causes of the H₃ hysteresis loop due to the adsorption of composite material are because of the hole wall of multilayer adsorption and condensation, two factors in the hole, by the action of the stripping process caused only by capillary condensation. Given the multilayer structure for a parallel state, Kelvin radius changes constantly, thus resulting in the H₃-type hysteresis phenomenon. The BET (Brunauer-Emmett-Teller) equation was used to analyze the data, and its specific surface area was 568.35 m²/g. Figure 7B shows the pore size distribution of molybdenum disulfide/biological structure carbon composites prepared by the hydrothermal calcination method with the concentration of molybdenum chloride of 0.20 mol/L. It can be concluded from the figure that the nano-pore size of the composite is between 2 and 20 nm, which further proves that the material is a mesoporous system. It was observed that the ratio of 4 nm mesopores in the material system was high, which was caused by the coordination between pores in the carbon mesosphere of biological structure and flake MoS₂.

Photocatalytic Decomposition of Water to Produce Hydrogen

Figure 8 shows the hydrogen evolution of MoS₂/C composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L under visible light irradiation for three cycles. In addition to four samples with different concentrations of molybdenum chloride, pure MoS₂ was also tested in the photocatalytic decomposition of water to produce

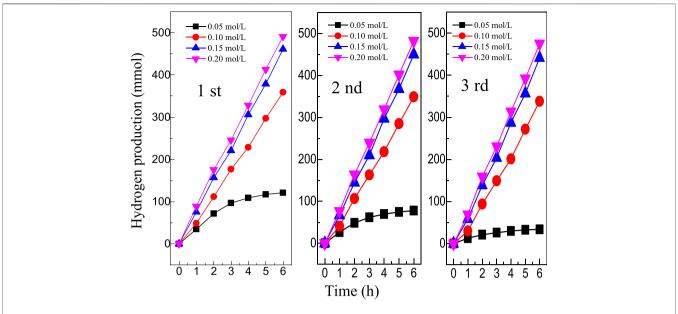


FIGURE 8 | Hydrogen evolution of MoS₂/C composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L under visible light irradiation for three cycles.

hydrogen. The experimental results show that MoS2 can hardly decompose water to produce hydrogen. The photocatalytic performance of the composite system with a higher concentration (0.10, 0.15, and 0.20 mol/L) was better than that of the composite system with a lower concentration (0.05 mol/L) in each cycle experiment. After 6 h of illumination, the hydrogen production of low concentration MoS₂ composites tended to be gentle, while the hydrogen production of the three high concentration composites showed an upward trend. Comparing the results of three cycles, it can be found that the hydrogen production of the MoS₂ sample with the concentration of 0.05 mol/L decreases significantly with the increase of the number of cycles, while the photocatalytic hydrogen production of composite materials with other concentrations still reaches a stable high value after multiple cycles. This is because MoS₂ has a more serious photocorrosion phenomenon when the concentration is low, which limits the continuous photocatalytic reaction. After 6 h of illumination in the first cycle, the photocatalytic decomposition of hydrogen in aquatic products with four concentrations were 120.85, 358.95, 464.02, and 492.12 µmol, respectively. The hydrogen production of MoS₂/C composites prepared by the hydrothermal calcination method with the different concentrations of molybdenum chloride including 0.05, 0.10, 0.15, and 0.20 mol/L were 32.61, 336.40, 443.27, and 475.14 µmol, respectively, after 6 h of illumination in the third cycle.

Due to the low band gap value of MoS₂ and the introduction of biological structure carbon particles, the band gap value of the system is further reduced so that when the light shines on the surface of the composite material, the electrons in the MoS₂ band are easy to undergo transition to the conduction band of MoS₂ under the action of biological structure carbon (Wang and Zhao, 2019; Li et al., 2020; Deng et al., 2021; Ibrayev et al., 2021; Pu et al.,

2021; Sharma et al., 2021; Syed et al., 2021; Xiu et al., 2021; Yang et al., 2021; Wang et al., 2021d). Biological structure carbon accelerates the transfer rate of charge carriers between the conduction band and the valence band of MoS2, thus enhancing the transfer and separation efficiency of charge carriers in the system. Therefore, the photocatalytic activity of MoS₂/C composites was mainly attributed to the high charge transfer and separation efficiency of the system. The photogenerated electron in MoS₂/C composites can effectively reduce the water molecule to produce OH and give off H₂ (Yu et al., 2011; Zhang et al., 2013). In addition, the water molecule can be oxidized by hole to produce H⁺ and to release O₂ (Zhang et al., 2013). It is also possible as the competition between the recombination of the electron-hole pair and the charge transfer and separation reaction occur in pure water. The backreaction between H₂ and O₂ produces water on the surface of MoS₂/C composites (Husin et al., 2011). The change of the band gap value continuously regulates the electron migration and recombination rate of MoS₂/C composites and then influences its hydrogen production ability.

CONCLUSION

Four kinds of MoS₂/C photocatalytic composites with different concentrations of molybdenum chloride were prepared by the hydrothermal calcination method using bamboo leaves as the biological template, thiourea as the sulfur source, and molybdenum chloride as the molybdenum source. TG-DSC, XRD, SEM, TEM, UV-VIS DRS, PL, and gas chromatograph were used to systematically study the thermal decomposition behavior, phase purity, surface morphology, optical properties, photoluminescence properties, and photocatalytic decomposition

of water to produce hydrogen of MoS₂/C photocatalytic composites with different concentrations of molybdenum chloride. The experimental results show that the hydrothermal calcination method can be used to load MoS₂ onto the biological carbon and form a structurally stable composite system. The MoS₂/C composites prepared by the hydrothermal calcination method with the concentration of molybdenum chloride of 0.20 mol/L exhibits a high charge transfer and separation efficiency. With the increase in the concentration, the photocatalytic activity of the material was significantly improved, and it showed excellent photocorrosion resistance and recyclability, which provided an effective synthesis approach for the preparation of MoS₂/C composites with a stable photocatalytic performance.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

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AUTHOR CONTRIBUTIONS

SW and JD were responsible for synthesis experiments and the TG-DSC test. CW was responsible for performance tests and data analysis. WL was responsible for the analysis and guidance of XRD, SEM, and TEM. ZC was responsible for analyzing the reaction mechanism. CL and FC were responsible for the experimental design and manuscript revision.

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