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A Floating Triphase Photothermal Platform: MoS_2/SnS_2 on Fly Ash for Efficient CO_2 Reduction and Tetracycline Degradation

Ming Cai[a, b], Wenwen Li[a], Ebtihal Abograin[b], Yan Guo[d], Xu Tang[c], Zhi Zhu[b,*], Ming Feng[a,*], Pengwei Huo[b]

a. Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, China
b. School of Chemistry and Chemical Engineering, Institute for Advanced Materials, Jiangsu University, Jingjiang College, Jiangsu University, Zhenjiang 212013, PR China
c. Institute for Advanced Materials, Jiangsu University, Zhenjiang 212013, PR China
d. School of Automotive Engineering, Changzhou Institute of Technology, Changzhou 213032, China

Corresponding authors:

Z. Zhu (zhuzhi@ujs.edu.cn), M.Feng (mingfeng@jlnu.edu.cn)

1. Experimental section

1.1 Materials and chemicals

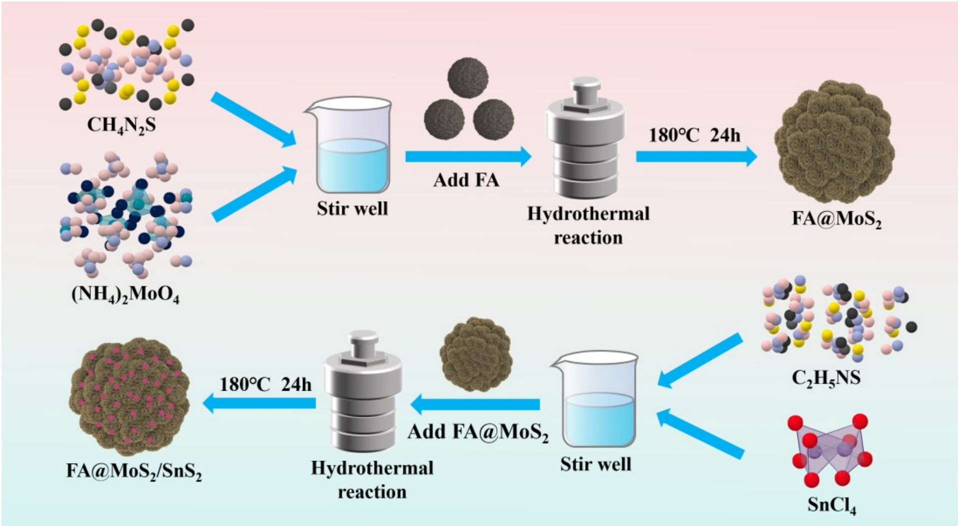
All reagents were used as received without further purification. The coal FA substrate was collected from the electrostatic precipitator of a coal-fired power plant. Tetracycline (TC, ≥98%) was supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. (China). Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 99.5%), thiourea ($CH_4N_2S$, 99%), tin(IV) chloride pentahydrate ($SnCl_4\cdot 5H_2O$, 99%), thioacetamide (C_2H_5NS, 99%), and absolute ethanol (99.7%) were procured from Shanghai Macklin Biochemical Technology Co., Ltd. The FA was pre-washed with 1 M HCl to remove soluble impurities and dried at 80 °C for 12 h before use, ensuring a clean surface for heterojunction growth.

1.2 Synthesis of MoS_2-FA Composites

The MoS_2-FA composite was synthesized through a two-step hydrothermal method designed to achieve uniform growth of MoS_2 nanosheets on FA microparticles. The process begins with pretreatment of FA to activate its surface, typically involving washing with HCl to remove soluble impurities and enhance surface reactivity. The activated FA microparticles are then dispersed in an aqueous solution containing a molybdenum source ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and a sulfur source ($CH_4N_2S$). This mixture undergoes hydrothermal treatment at temperatures ranging from 180°C for 24 hours in a Teflon-lined autoclave. The resulting composite is collected by centrifugation, washed thoroughly, and dried at 60°C to yield the final MoS_2-FA material.

1.3 Synthesis of MoS_2/SnS_2-FA Composites

The MoS_2/SnS_2-FA was obtained by subjecting the as-prepared MoS_2-FA to a second hydrothermal reaction with tin(IV) chloride pentahydrate and thioacetamide as Sn and additional S sources at 180°C for 24 h, enabling the in situ epitaxial growth of SnS_2 nanosheets onto the MoS_2-modified FA substrate. This facile process resulted in the formation of an intimate type-II heterojunction with enhanced interfacial charge separation and photothermal properties, as confirmed by structural and electrochemical analyses.



Scheme 1. Synthesis diagram of MoS_2/SnS_2-FA.

1.4 Characterizations

A comprehensive suite of characterization techniques was employed to probe the material's properties. X-ray diffraction (XRD) analysis was conducted on a Shimadzu-6100 diffractometer equipped with a Cu Kα radiation source, employing a scanning scope from 10° to 90° (2θ) at a rate of 10° per minute. Chemical states and elemental composition were assessed via X-ray photoelectron spectroscopy (XPS) using a Shimadzu/Krayos AXIS Ultra DLD instrument. Morphological examination was performed with a JEOL JSM-7001F field-emission scanning electron microscope (FE-SEM). Optical properties were evaluated by ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) on a Shimadzu UV-3600 spectrophotometer, while photoluminescence (PL) emission spectra for solid powders were recorded using a Hitachi F4500 fluorescence spectrometer with a 375 nm xenon lamp excitation source. The pathway of CO_2 photoreduction was monitored through in situFourier transform infrared (FTIR) spectroscopy on a Thermo Fisher Nicolet iS-10 spectrometer. Quantification of TC throughout the reaction process was achieved through ultraviolet-visible spectroscopic analysis at specific absorption wavelengths, with structural identification of transient intermediates performed via high-resolution mass spectrometry. Surface temperature distribution under illumination was captured with an infrared thermal imager. Furthermore, electrochemical characteristics, including electrochemical impedance spectroscopy (EIS) and transient photocurrent response (TPR), were measured to investigate charge carrier dynamics.

1.5 CO_2 Photoreduction Experiments

The photocatalytic reduction of carbon dioxide was evaluated in a specialized 100 mL sealed quartz reactor under irradiation from a 300 W xenon lamp source, which supplied an incident light intensity of 1000 mW cm^{-2}. In a standard protocol, 50 mg of the MoS_2/SnS_2-FA composite was homogeneously dispersed on 10 mL of deionized water within the reactor. Prior to light exposure, high-purity CO_2 was continuously purged through the system for 20 minutes to fully displace atmospheric gases and establish an inert environment. The resulting gaseous products (CO, CH_4, H_2) were identified and quantified using an Agilent 5890 N gas chromatograph equipped with a flame ionization detector (FID) and a methanizer. Quantification was performed via external calibration using certified standard gas mixtures, and the detection limits for CO and CH_4 were determined to be below 0.5 μmol g^{-1} h^{-1} under the employed experimental conditions.

1.6 Photocatalytic degradation of TC test

The photodegradation of TC was evaluated using a custom 100 mL quartz reactor irradiated with a 300 W Xe lamp, delivering an incident light intensity of 1000 mW·cm^{-2}. In a typical experiment, 50 mg of MoS_2/SnS_2-FA catalyst was dispersed in 20 mL of an aqueous TC solution (20 mg·L^{-1}). The suspension was magnetically stirred in darkness for 30 minutes to achieve adsorption–desorption equilibrium, with samples taken at 10-minute intervals. After filtration, the supernatant was analyzed by UV-vis spectrophotometry to quantify TC concentration based on its characteristic absorption peak at 358 nm. Upon illumination, aliquots were collected periodically under identical sampling conditions to monitor degradation kinetics. For recyclability studies, the MoS_2/SnS_2-FA catalyst was recovered after each cycle via centrifugation, washed thoroughly with deionized water, dried, and reused under consistent experimental settings.

1.7 Photo-electrochemical measurements

The working electrodes were fabricated by subjecting MoS_2-FA and MoS_2/SnS_2-FA powders to mechanical grinding to achieve fine particulate forms. A precise mass of 0.05 g of each sample was homogenously suspended in 3.0 mL of ethanol, followed by the incorporation of 0.03 mL oleic acid and 0.01 g polyvinylpyrrolidone (PVP) as film-forming additives. This mixture was then deposited onto fluorine-doped tin oxide (FTO) substrates (1×1 cm^2) via spin-coating and air-dried under ambient conditions. Electrochemical analyses were conducted in a standard three-electrode configuration employing a platinum wire counter electrode, a saturated calomel reference electrode (SCE), and 0.5 M Na_2SO_4 aqueous electrolyte. Measurements were carried out with a Chen Hua electrochemical station applying a 5 mV sinusoidal potential perturbation, and the resulting data were acquired and processed using a CHI660B electrochemical analyzer (Chen Hua Instruments, Shanghai, China).