Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Noble-metal-free MoS_2 nanosheets modified-$InVO_4$ heterostructures for enhanced visible-light-driven photocatalytic H_2 production

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Experimental section

General Procedures: Indium chloride ($InCl_3$), ethanolamine, ammonium vanadate (NH_4VO_3), sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$), thiourea, ethanol and methanol were obtained from Mike Chemical Reagent Co., Ltd Cd. All reagents were used as received without further purification.

Characterization: Powder X-ray diffraction (XRD) patterns were performed on a Rigaku D/Max-2550pc powder diffractometer equipped with Cu-Ka ($\lambda = 0.15406$ nm) radiation in the 2θ ranging from 10^o to $80\ ^o$ with a scan rate of 10^o per minute. The optical properties of the products were characterized by a Varian Cary 500 UV-vis spectrophotometer, in which $BaSO_4$ was used as the internal reflectance standard. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a VG ESCALAB MKII XPS system with Al Kα X-ray source and a charge neutralizer. The morphology of the photocatalysts was determined by using a field-emission scanning electron microscopy (FE-SEM, vltra55), high-resolution transmission electron microscopy (HR-TEM, JEM 2010) with an accelerating voltage of 200 kV. The SEM and TEM samples were obtained by depositing a drop of diluted suspensions in ethanol on a silicon chip and carbon-film-coated copper grid, respectively. Raman spectra of products were recorded at room temperature using Raman spectrometer (J-Y T64000) in the backscattering geometry with 514.5 nm wavelength incident laser light.

Preparation of $InVO_4$.

In a typical synthesis of $InVO_4$, 1 mmol of $InCl_3$ and 1 mmol NH_4VO_3 were dissolved in 60 mL of distilled water containing 10 mM ethanolamine, which was then transferred into a 100 mL Teflon-lined autoclave and kept at 150 ^oC for 16 h. After that, the green precipitate was collected by centrifugation, washed two times with distilled water and ethanol, and then dried in an oven at 60 ^{o}C for 12 h.

Preparation of $MoS_2/InVO_4$ photocatalysts.

In a typical synthesis of $MoS_2/InVO_4$ composite photocatalyst, 500 mg of the prepared $InVO_4$ was sonicated thoroughly in 50 ml aqueous solution containing 7.5 mg $Na_2MoO_4{\bullet}2H_2O$ and 15 mg thiourea. Next, the heterogeneous solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 200 ^{o}C for 24 h. After the reaction solution was cooled to room temperature, the grey precipitate was separated by centrifugation, washed three times with absolute ethanol, and then dried in an oven at 60 ^{o}C to obtain 1 wt% $MoS_2/InVO_4$ sample. In order to investigate the effect of MoS_2 content in the $MoS_2/InVO_4$ composite photocatalysts on the photocatalytic H_2 evolution activity, the weight percentages of MoS_2 to $InVO_4$ were varied from 0 to 5 (0, 1, 2, 3, 4 and 5 wt%) by varying the weight of $Na_2MoO_4{\bullet}2H_2O$ and thiourea (2 equiv of $Na_2MoO_4{\bullet}2H_2O$), the resulting samples were annealed at 400 ^{o}C for 3 h under nitrogen atmosphere.

Photocatalytic H_2 production.

The photocatalytic H_2-evolution experiments were performed in a 350 mL Pyrex flask, which was connected to a closed gas-circulation lation glass system. H_2 production experiments experiment was performed by dispersing 100 mg powder photocatalyst in 250 ml aqueous solution containing methanol (20%, V/V) as sacrificial electron donor. After the solution was degassed to remove air completely, the mixture solution was irradiated by a 300 W Xe lamp equipped with a cut-off filter ($\lambda > 420$ nm) with gentle magnetic stirring. The evolving H_2 were periodically detected in situ on a gas chromatograph (Jiedao GC1690, TCD, argon as a carrier gas and MS-5A molecular sieve column). The standard errors in the photocatalytic H_2 evolution performance for all photocatalytic experiments were less than 2.0%.

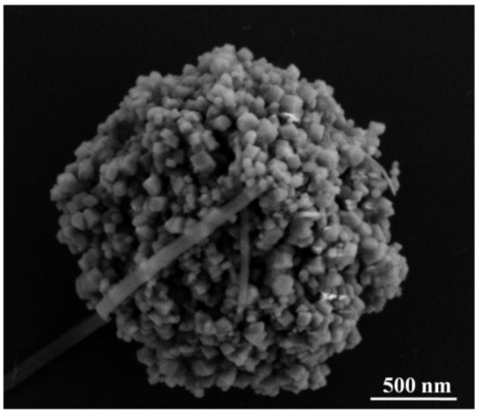

Fig. S1 SEM image of pure $InVO_4$ sample.

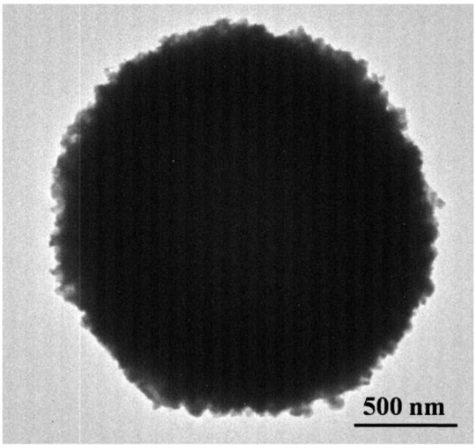

Fig. S2 TEM image of pure $InVO_4$ sample.

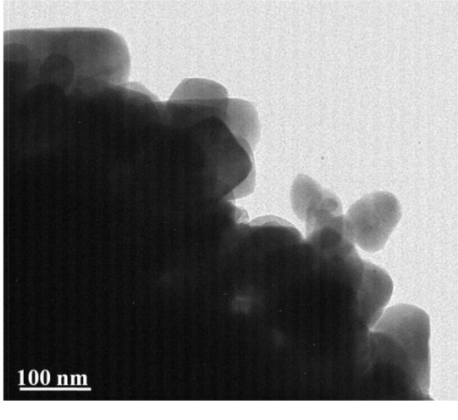

Fig. S3 TEM image of pure $InVO_4$ sample.

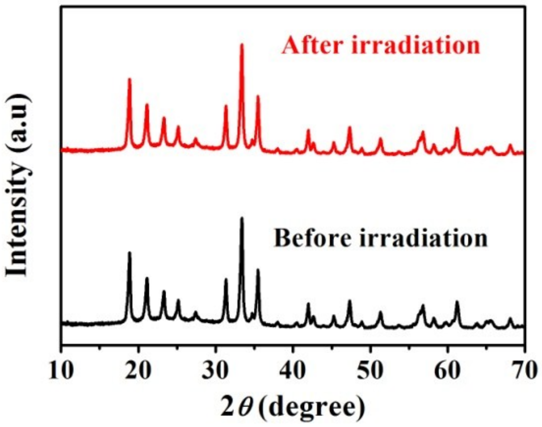

Fig. S4 X-ray diffraction patterns for 3 wt% $MoS_2/InVO_4$ photocatalyst before and after visible light irradiation.