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Supplementary materials

ZnO/ZnS-Polyvinyl Alcohol Hydrogel for Photocatalytic H_2-Generation

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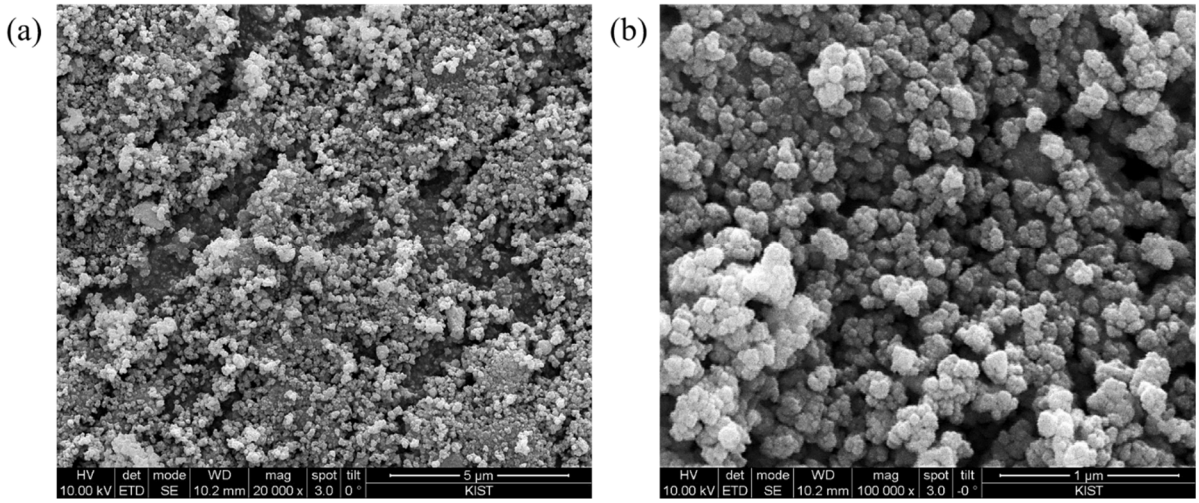

Figure S1. SEM images of ZnOS nanoparticles at (**a**) low resolution and (**b**) high resolution.

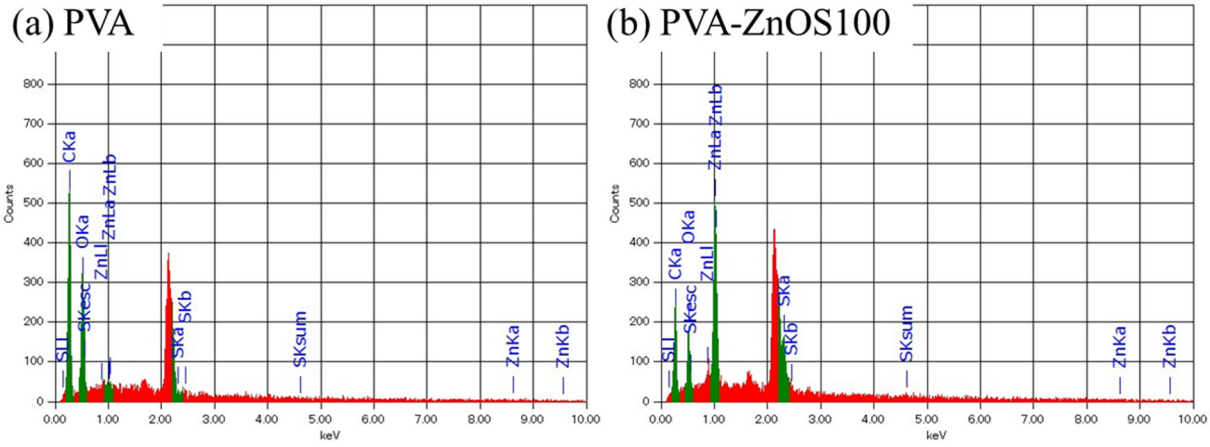

Figure S2. EDS spectra of (**a**) pure PVA and (**b**) PVA-ZnOS100 composite.

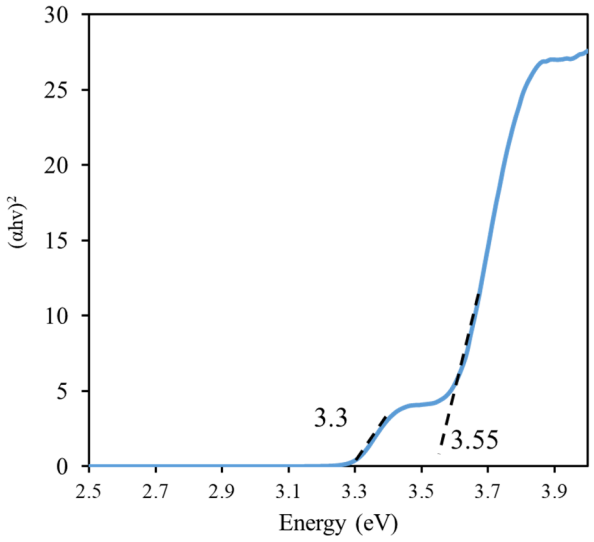

Figure S3. Bandgap energy from Tauc plot obtained from UV-vis absorption spectrum of ZnOS.

Table S1. Decomposition temperature and weight loss (W.L.) obtained from TGA analysis.

Sample	Stage 1		Stage 2		Stage 3		Residual (%)	Particle (%)
	Tem. (°C)	W.L. (%)	Tem. (°C)	W.L. (%)	Tem. (°C)	W. L. (%)		
PVA	<212	5	212-371	79	412-460	15	1	0
PVA-ZnOS100	<159	5	159-335	63	405-452	27.07	4.93	3.93
PVA-ZnOS150	<159	5	159-258	56	345-488	30.48	8.52	7.52
PVA-ZnOS200	<212	5	212-269	55	351-485	29.17	10.83	9.83

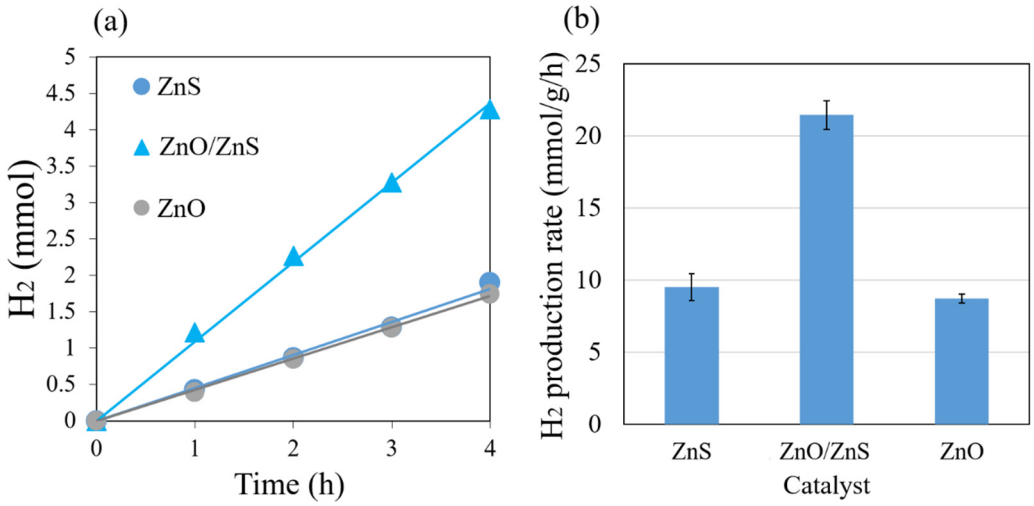

Figure S4. (a) H_2 generation as a function of radiation time from ZnS, ZnO/ZnS, and ZnO nanoparticles; (b) average production rate of H_2 of all samples under the UV light irradiation.

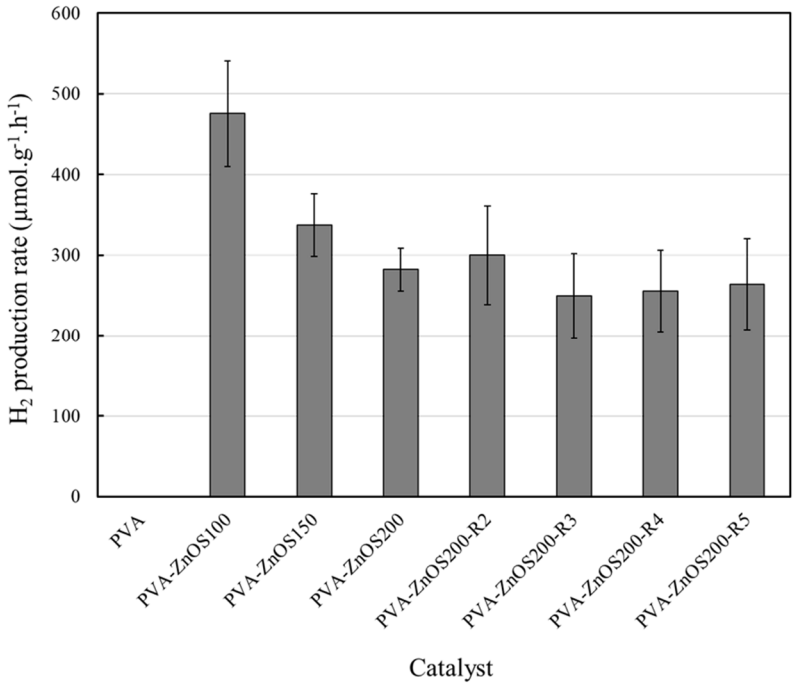

Figure S5. Hydrogen production rates in $\mu mol \cdot g^{-1} \cdot h^{-1}$.

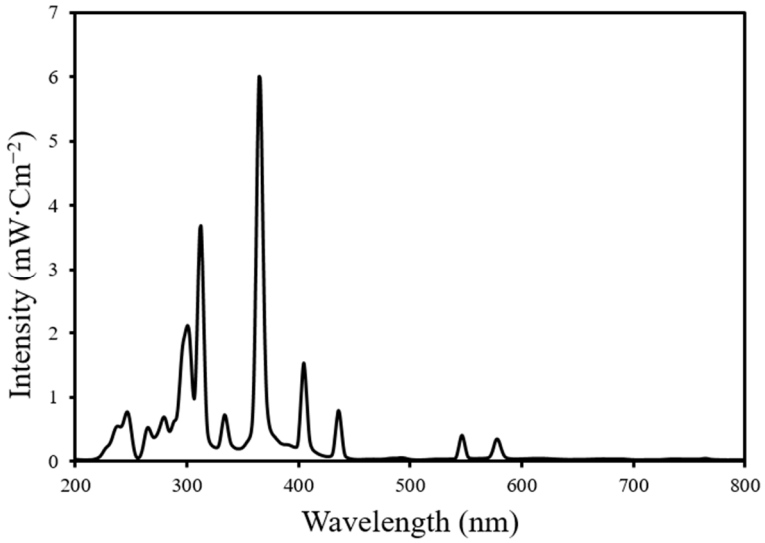

Figure S6. Radiation spectrum of Xe-Hg lamp used in this experiment.

Table S2. Photocatalytic activities for H_2 generation with previous reports (for comparison, production rates were normalized per gram catalyst).

Materials	Reaction	Catalyst (mg)/Solution (mL)	H_2 rate ($\mu mol.g^{-1}.h^{-1}$)	Recyclability	Ref
PVA-ZnOS-100	Xe-Hg lamp, (200~400 nm = 146 $mW.Cm^{-2}$)/Na_2S-Na_2SO_3	33/50	475	Separation free	This work
PVA-ZnOS-150		50/50	337		
PVA-ZnOS-200		66/50	282		
PVA-ZnOS-200-R5		66/50	263		
$CdS/HGel_{PDAM}$	450 W Hg -lamp (>380 nm)/ Na_2S-Na_2SO_3	5/11	7700	Separation needed	[1]
Pt/CdS/SiO_2/PANI	500 W Xe-lamp (>320 nm, 80 $mW.cm^{-2}$)/Lactic acid	15/30	14160	NA	[2]
Pt/C_3N_4/polymer hydrogel	300 W Xe-lamp (0.7 $mW.cm^{-2}$ at 420 nm)/TEOA	10/100	7427	Separation free	[3]
Pt/Ag-C_3N_4/melamine hydrogel	300 W Xe-lamp (>420 nm)/TEOA	50/100	625	NA	[4]
Pt/N-TiO_2/$SrTiO_3$/PVA	Xe-lamp (312 $W.m^{-2}$)/methanol	NA/50	34895	NA	[5]

For comparison, we have selected recent works related to polymer hydrogel photocatalysts for hydrogen generation and summarized their hydrogen production rates in Table S2. Li et al. prepared CdS embedded into dimethylaminoethyl methacrylate/acrylamine hydrogel ($CdS/HGel_{PDAM}$) and used it for H_2 generation from an Na_2S/Na_2SO_3 solution under UV from a Hg-lamp. The hydrogen production rate was up to 7700 $\mu mol \cdot g^{-1}h^{-1}$, which is much higher than our samples. Since no light intensity was reported there, we are unsure how intense their light was [1].

Lu et al. synthesized composite structure of CdS nanorod-SiO_2 photocatalyst embedded into polyaniline hydrogel (Pt/CdS/SiO_2/PANI) and performed photocatalytic H_2-generation from lactic acid solution with Pt as a cocatalyst under a Xe-lamp. The production rate was very high: ~14160 $\mu mol \cdot g^{-1}h^{-1}$. This extremely high hydrogen production rate was mainly due to the noble cocatalyst [2]. Although these catalysts showed greater activity in hydrogen generation, the use of an expensive cocatalyst and the toxicity of CdS are not good choices for industrial production.

Lei et al. loaded Pt atoms on C_3N_4 nanosheets and embedded them into polymer hydrogel (N-Isopropylacrylamide/N,N′-methylene bisacrylamine/sodium alginate). Photocatalytic H_2-generation was performed from triethanolamine (TEOA) solution under Xe-lamp with low intensity (0.7 $mW \cdot cm^{-2}$). The hydrogen production rate was ~7427 $\mu mol \cdot g^{-1}h^{-1}$. Hydrogel catalyst was used in film/gel and no separation was needed. Their hydrogel activity was much better than ours. However, noble metal was

still used in this work [3]. Wang et al. synthesized Ag/g- C_3N_4 melamine hydrogel composite. Photocatalytic H_2-generation performed well under visible light (>420 nm) with a Pt cocatalyst. The hydrogen production rate was 625 $\mu mol \cdot g^{-1}h^{-1}$. Although performance was high, noble metals such as Ag and Pt were not unavoidable. Furthermore, the catalyst used in the form of dry powder would require a process for separation [4].

Recently, Lee et al. prepared a complex compound composed of N-doped $TiO_2/SrTiO_3$ loaded Pt cocatalyst and embedded it into the PVA matrix. Photocatalytic H_2-generation was performed in methanol solution under Xe-lamp, and the H_2-production rate was up to 34895 $\mu mol \cdot g^{-1}h^{-1}$. It should be outstanding hydrogel-support catalyst compounds among selected works. However, multi-steps to synthesize this complex catalyst structure and the expensive metals required would not be eligible to compare with our samples. Although our sample produced a lower H_2-production rate, the process for synthesis is facile, and no noble metal was used.

References

1. Li, F.; Yang, J.; Gao, J.; Liu, Y.; Gong, Y. Enhanced photocatalytic hydrogen production of CdS embedded in cationic hydrogel. *Int. J. Hydrog. Energy* **2020**, *45*, 1969–1980.
2. Lu, J.; Zhang, X.; Gao, H.; Cui, W. Three-dimensional structure of PANI/CdS NRs-SiO_2 hydrogel for photocatalytic hydrogen evolution with high activity and stability. *Nanomaterials* **2019**, *9*, 427.
3. Lei, L.; Wang, W.; Wang, C.; Fan, H.; Yadav, A.K.; Hu, N.; Zhong, Q.; Buschbaum, P.M. hydrogel-supported graphitic carbon nitride nanosheets loaded with Pt atoms as a novel water-storage photocalyst forH_2 evolution. *J. Mater. Chem. A* **2020**, *8*, 23812–23819.
4. Wang, J.; Cong, J.; Xu, H.; Wang, J.; Liu, H.; Liang, M.; Gao, J.; Ni, Q.; Yao, J. Facile gel-based morphological control of Ag/g-C_3N_4 porous nanofibers for photocatalytic hydrogen generation. *ACS Sustain. Chem. Eng.* **2017**, *5*, 10633–10639.
5. Madhusudan, P.; Wang, Y.; Chandrashekar, B.N.; Wang, W.; Wang, J.; Miao, J.; Shi, R.; Liang, Y.; Mi, G.; Cheng, C. Nature inspired ZnO/ZnS nanobranch-like composites, decorated with Cu $(OH)_2$ clusters for enhanced visible-light photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **2019**, *253*, 379–390.