Supplementary Information

Atomically-thin two-dimensional ZnSe/ZnSe(ea)$_x$ Van der Waals nanojunction for synergistically enhanced visible light photocatalytic H_2 evolution

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AQE calculation

Calculated AQE at different wavelength of ZnSe/ZnSe(ea)$_x$.

λ (nm)	H_2 evolved(μ mol)	P*S (mW)	AQE (%)
450	133.12	304	64.50
500	84.88	510	22.00
550	62.38	670	11.20

When λ = 450 nm:

$$N_p = \frac{P*S*t}{hc/\lambda} = \frac{304\times10^{-3}\times3600\times450\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}} = 2.48\times10^{20}$$

$$N_e = 2\times M\times N_A = 2\times133.12\times10^{-6}\times6.02\times10^{23} = 1.60\times10^{20}$$

$$AQE = \frac{N_e}{N_p}\times100\% = 64.50\%$$

When λ = 500 nm:

$$N_p = \frac{P*S*t}{hc/\lambda} = \frac{510\times10^{-3}\times3600\times500\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}} = 4.64\times10^{20}$$

$$N_e = 2\times M\times N_A = 2\times84.88\times10^{-6}\times6.02\times10^{23} = 1.02\times10^{20}$$

$$AQE = \frac{N_e}{N_p}\times100\% = 22.00\%$$

When λ = 550 nm:

$$N_p = \frac{P*S*t}{hc/\lambda} = \frac{670\times10^{-3}\times3600\times550\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}} = 6.70\times10^{20}$$

$$N_e = 2\times M\times N_A = 2\times62.38\times10^{-6}\times6.02\times10^{23} = 7.50\times10^{19}$$

$$AQE = \frac{N_e}{N_p}\times100\% = 11.20\%$$

DFT calculation Details.

Our calculations are based on density functional theory (DFT) under the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional as implemented in the VASP code[1-3]. A plane wave basis set with the projector-augmented plane wave (PAW) was performed to describe the ion-electron interaction and the plane-wave cutoff energy was set to be 500eV.[4] The *k*-point mesh of 15×15×1 were generated according to the Monkhorst-Pack scheme for monolayer ZnSe (1×1) cell.[5] All the geometries were relaxed until the forces acting on each ion were smaller than 0.01 eV $Å^{-1}$, and the energy change was less than 10^{-5} eV. The Ethylamine was put on several different adsorption sites of ZnSe monolayer with different orientations to search for the most stable adsorption site. The electronic properties of ZnSe and $ZnSe(ea)_x$ are computed based on the HSE06 functional.[6]

Supporting Tables

Table S1 the Determination of coordination number.

sample	Total Zn+Se Mass percentage(%)	$ZnSe(amine)_x$/total Zn Molar percentage (%)	non-coordinated $ZnSe/ZnSe(amine)_x$	Coordinated ZnSe /total Zn+Se Mass ratio	Weight loss Mass percentage (%)	coordination number x
3-days& amine=ea	86.97	13.06	6.67	0.15	13	3.19
10-days& Amine=ea	87.38	12.62	6.92	0.14	14	3.61
6-days& Amine=ea	82.99	17.01	4.88	0.20	16	2.97
3 days& amine=Pa	75.14	24.86	3.02	0.33	22.77	2.17

Table S2. H_2 evolution rates of some representative photocatalysts without using any cocatalyst.

Photocatalyst	H_2 evolution rate ($\mu mol \cdot h^{-1} \cdot g^{-1}$)	Light source incident light
Ball-milled black phosphorus (BP-BM)[24]	512	300W Xe lamp / λ＞ 420 nm
Amorphous red phosphorus/crystalline red phosphorus[25]	0.6/1.6	300W Xe lamp / full spectrum
mesoporous crystalline Si[26]	400	300W Xe lamp / λ＞ 420 nm
g- C_3N_4 /carbon nanodots[27]	105	300W Xe lamp / λ＞ 420 nm
Phosphorus-doped g- C_3N_4[28]	670	300W Xe lamp / λ＞ 420 nm
g-C_3N_4 /S-Se-graphene[29]	2590	300W Xe lamp / λ＞ 420 nm
Oxygen-Doped $ZnIn_2S_4$ nanosheets[30]	2120	300W Xe lamp / λ＞ 420 nm

Supporting Figures

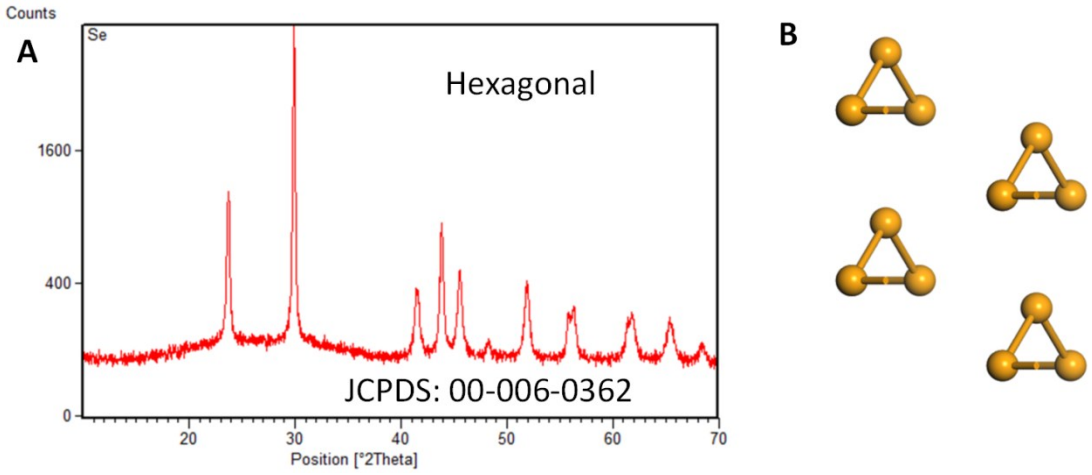

Figure S1. (A) XRD pattern and (B) Projection Se crystal structure along the z-axis.

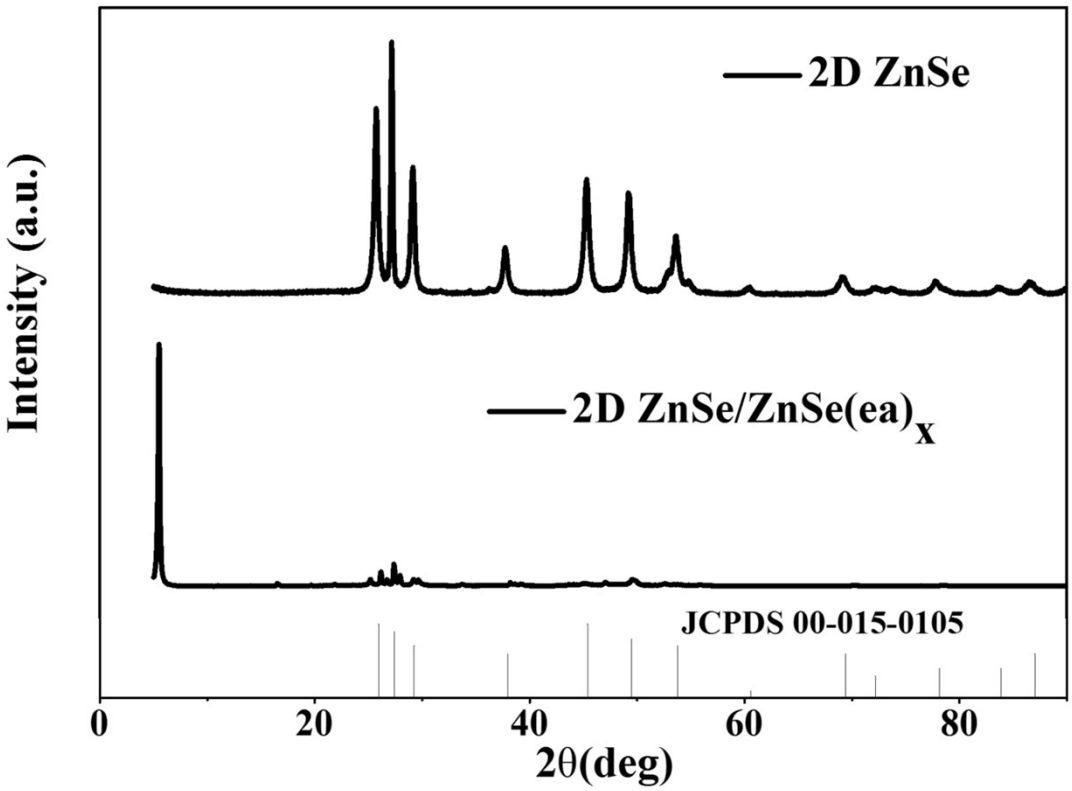

Figure S2. The XRD pattern of 2D/2D ZnSe/ZnSe(ea)$_x$ VDW nanojunction and pure 2D ZnSe nanosheets.

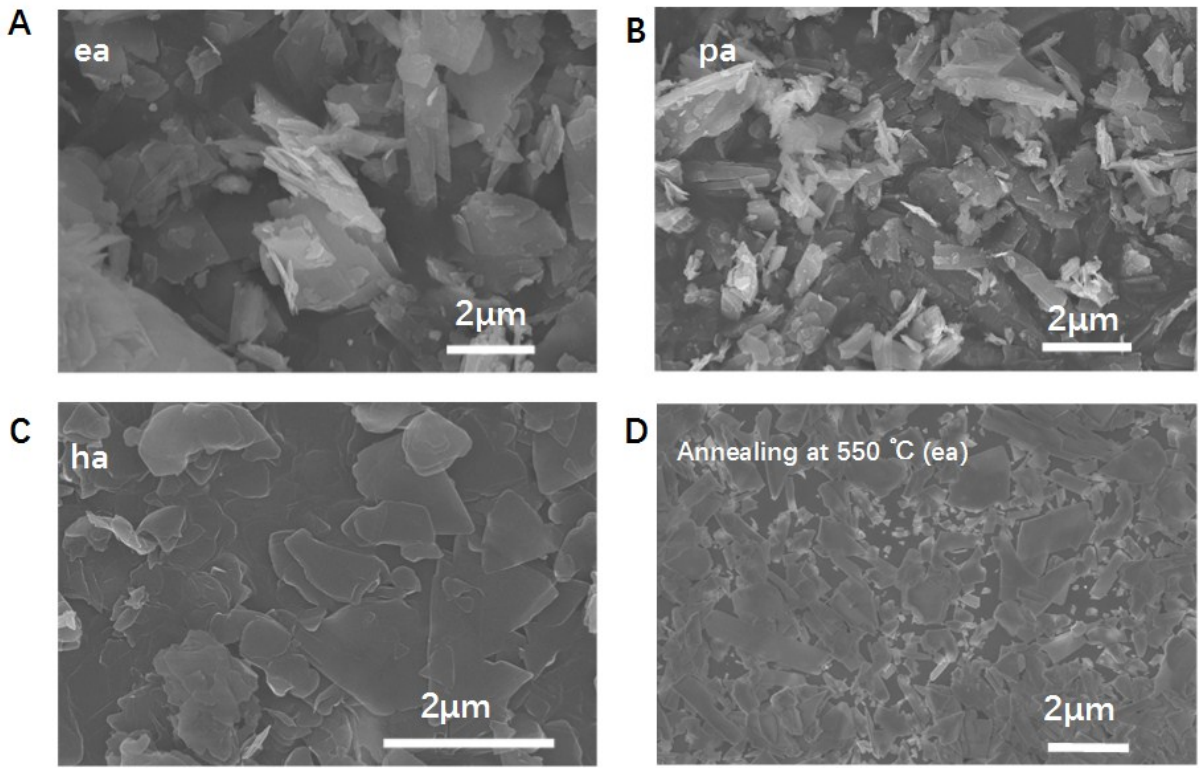

Figure S3. SEM images of 2D/2D ZnSe/ZnSe(ea)$_x$ (A) 2D/2D ZnSe/ZnSe(pa)$_y$, (B) 2D/2D ZnSe/ZnSe(ha)$_z$, (C) and 2D ZnSe sample (D).

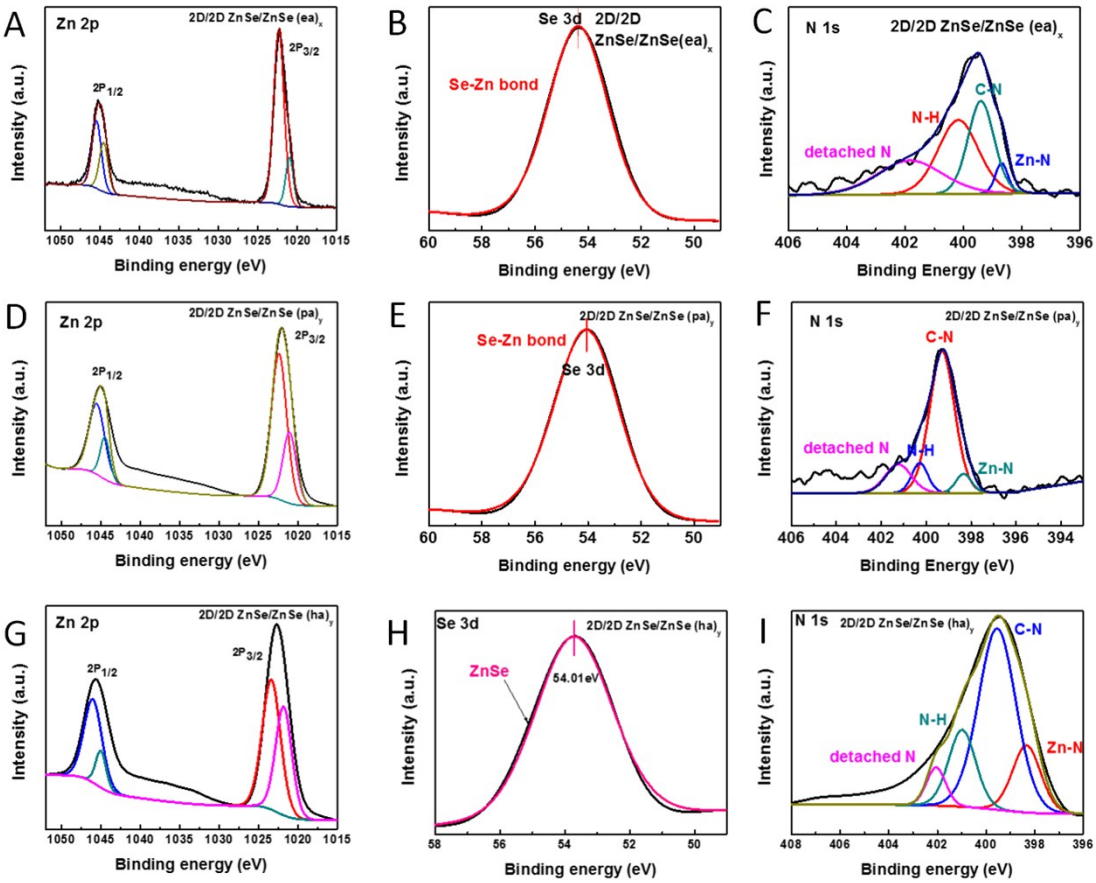

Figure S4. High-resolution XPS spectra of Zn 2p , Se 3d , N 1s in 2D/2D ZnSe/ZnSe(ea)$_x$ (A-C), 2D/2D ZnSe/ZnSe(pa)$_y$ (D-F), 2D/2D ZnSe/ZnSe(ha)$_z$ (G-I).

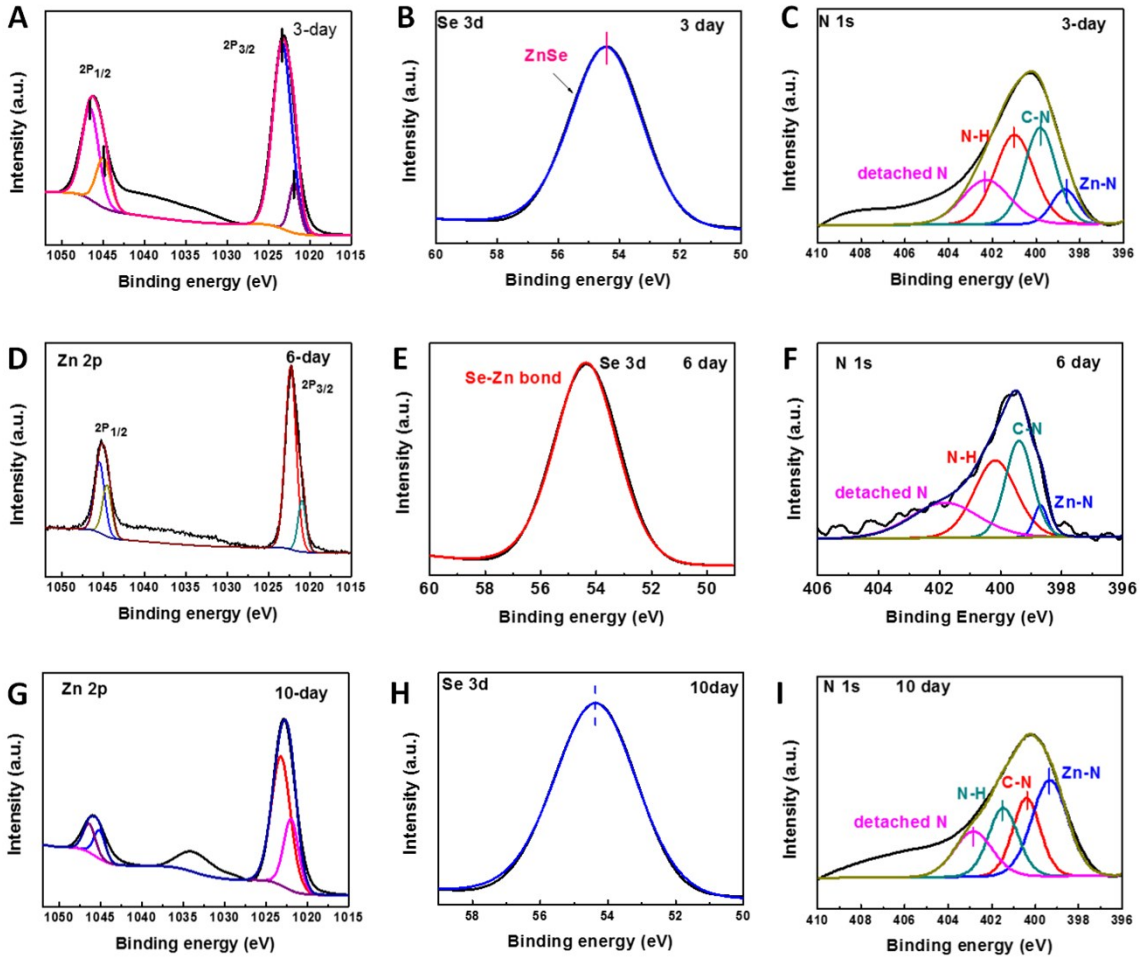

Figure S5. High-resolution XPS spectra of Zn 2p, Se 3d, N 1s in ZnSe/ZnSe(ea)$_x$ samples attained after different reaction days (A-C, 3-days, D-F, 6-days, G-I, 10-days).

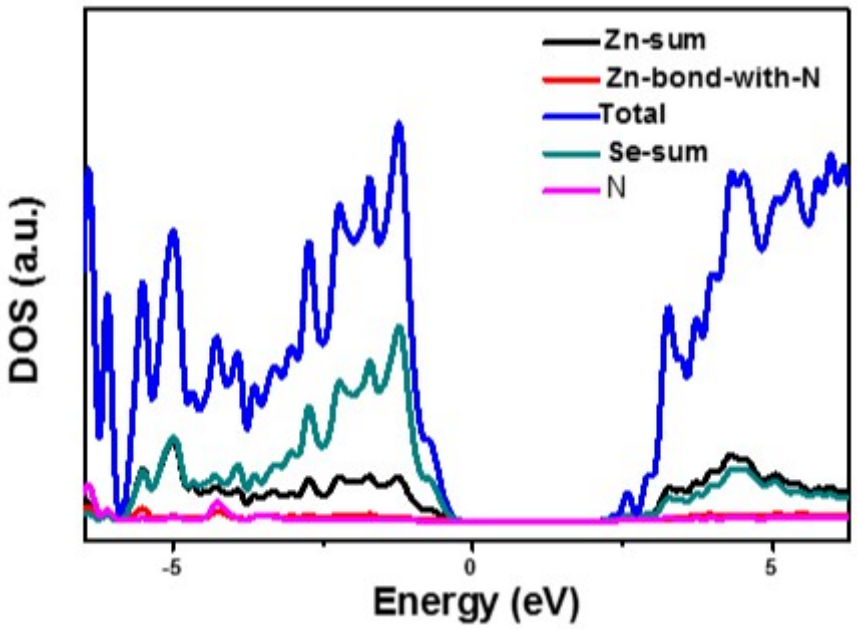

Figure S6. The calculated DOS for $ZnSe(ea)_x$. DOS=density of states.

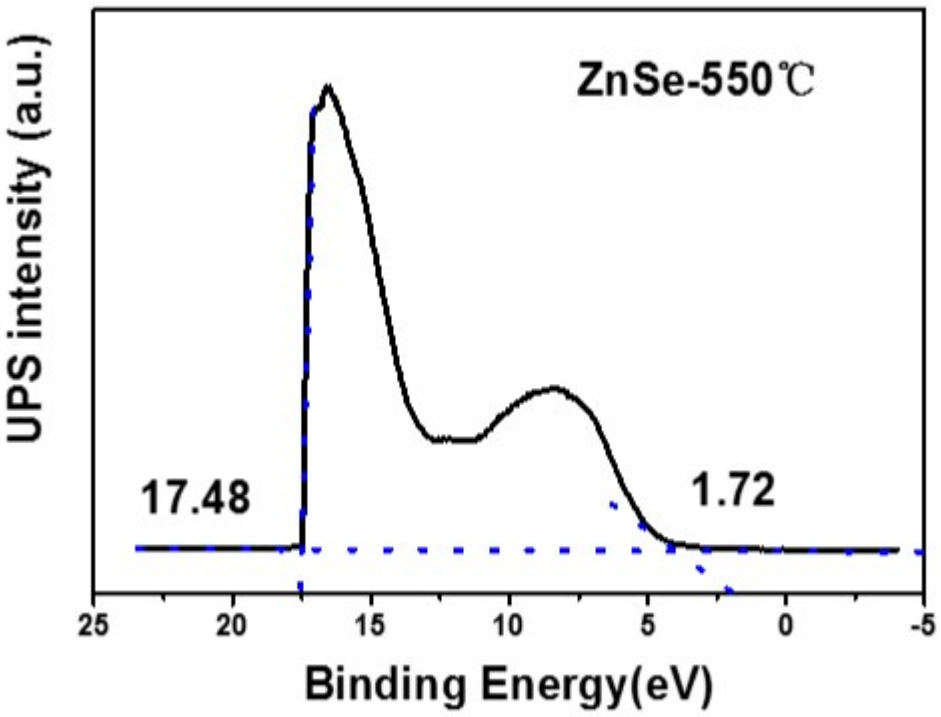

Figure S7. UPS spectrum of pure 2D ZnSe.

References

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