Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Material

Size-controlled growth of ZnSe nanocrystals for high-performance photocatalytic H_2O_2 production in pure water

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1. Experimental section

Synthesis of $Bi2Se_3$

$Bi2Se_3$ nanoparticles were prepared by a one-step solvothermal approach. Initially, 0.29 g potassium borohydride (KBH_4) was dissolved in a mixed solution (20 mL of deionized water and 5 mL of ethanol) at room temperature. Next, 0.29 g selenium (Se) powder was added to the above solution with constant stirring under nitrogen protection to form an optically transparent solution. The Se source solution containing KHSe was then obtained. At the same time, 0.59 g Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) was dissolved in 10 mL of deionized water to form a Bi source solution. Then the precursors were transferred to a Teflon-lined autoclave (50 mL), and heated at 180 °C for 12 h. Finally, the product was washed 3 times with absolute ethanol and distilled water, and then dried in a vacuum oven at 80 °C overnight.

Synthesis of ZnS

$ZnSO_4{\bullet}7H_2O$ (1.320 g) was added into 20 mL of DMSO under stirring for about 20 min until completely dissolved. Then 0.3500 g of thiourea was introduced into the solution and stirring for another 20 min.Then the precursors were transferred to a Teflon-lined autoclave (50 mL), and heated at 180 °C for 12 h. Finally, the product was washed 3 times with absolute ethanol and distilled water, and then dried in a vacuum oven at 80 °C overnight.

Synthesis of AgI

$AgNO_3$ (0.1447 g) was added into 100 mL of deionized water under stirring for about 20 min until completely dissolved. Then 0.1414 g of KI was introduced into the solution and stirring for another 20 min. The obtained product was rinsed 3 times with deionized water and ethanol, respectively. After being dried at 80 °C for 12 h in vacuum, light yellow powders of AgI were collected.

Synthesis of Nb_2O_5

Nb_2O_5 was prepared according to our former investigation [1]. In a typical process, $C_{10}H_5NbO_{20}$ (1.076 g) was dissolved in distilled water (30 mL) with stirring at 60 °C for 30 min until the solution became clear. The transparent solution was then sealed into a 50 mL Teflon-lined autoclave and heat-treated at 180 °C for 24 h. After the completion of the reaction, the precipitate was collected by centrifugation and washed repeatedly with distilled water. Subsequently, it was dried and collected for further use.

Synthesis of g-C_3N_4

Pure g-C_3N_4 powders were prepared by directing calcining urea in a muffle furnace. In a typical synthesis run, 10 g of urea was placed in an alumina crucible with a cover. The crucible was heated to 550 °C for 2 h with a heating rate of 2 °C·min^{-1}. After cooling to room temperature, g-C_3N_4 was obtained in a powder form.

Apparent quantum efficiency (AQE) calculations [2].

The apparent quantum efficiency can be evaluated from equation (1):

$$AQY = N_{(H2O2)} \times 2 / N_{(Photons)} \times 100\% \qquad (1)$$

in which $N_{(H2O2)}$ and $N_{(Photons)}$ referred to the molecular number of generated H_2O_2 in unit time and the number of incident photons in unit time, respectively. The photocatalytic systems with 20 mg catalyst and 50 mL O_2 saturated aqueous solution containing 10 vol% isopropanol were irradiated for 1h at room temperature and atmospheric pressure, without any sacrificial reagents. The irradiated area is 7.065 cm^2. The resulting

AQE values are listed in the Table S2.

Photoelectrochemical measurements

Electrochemical measurement was performance on an electrochemical workstation (Shanghai Chenhua Ins.c) by using three-electrode system in 0.2 M Na_2SO_4, among which ZnSe coated L-type glassy carbon electrode with the loading mass of 0.24 mg/cm^2 served as working electrode while Pt foil and Ag/AgCl (3.5 M KCl) were utilized as counter and reference electrodes, respectively. Photocurrent response was obtained by measuring chronoamperometric curve at - 0.2 V vs. Ag/AgCl under a 300 W halogen lamp irradiation. The electrochemical impedance spectra (EIS) were conducted at open circuit potential and the frequency of 1000 Hz. To obtain Mott–Schottky curve of as-obtained samples, impedance-potential curve was achieved at -1.0 V to 1.0 V potential range.

Rotating disk electrode (RDE) measurements

The electrocatalytic properties of the oxygen reduction reaction (ORR) were studied using rotating ring-disk electrode (RRDE, PINE Research Instrumentation) analysis in O_2-saturated 0.2 M phosphate buffer solution (pH = 7). The working electrode was prepared as following: 2.2 mg of catalyst, 2.2 mg of XC-72, 20 μL of Nafion alcohol solution (5 wt %, Aldrich), 397.5 μL of deionized water, and 132.5 μL of 2-propanol were mixed and sonicated to form a uniform catalyst ink. Then 3.5 μL of ink solution was transferred onto the glassy carbon (GC) electrode and dried for the following test. During the whole test process, O_2 was kept flowing on the liquid surface of the electrolyte. The average transfer electron number (n) in the overall O_2 reduction was obtained by the slopes of Koutecky-Levich plots with the following equation:

$$j^{-1} = j_k^{-1} + B^{-1}\Omega^{-1/2}$$

$$B = 0.2nF\nu^{-1/6}CD^{2/3}$$

where j, j_k and Ω are the tested current density, kinetic current density and rotating speed (rpm), respectively. F and ν are the Faraday constant (96485 C mol^{-1}) and kinetic viscosity of water (0.01 cm^2 s^{-1}), C is the bulk concentration of O_2 in water (1.26×10^{-6} mol cm^{-3}) and D is the diffusion coefficient of O_2 (1.93×10^{-5} cm^2 s^{-1}).

Table S1. Photocatalytic H_2O_2 production under simulated sunlight irradiation catalyzed by ZnSe synthesized from different amounts of Se and KBH_4 at 180 °C. Reaction conditions: V_{H2O} = 45 mL, V_{IPA} = 5 mL; light intensity: 100 mW·cm^{-2}; temperature: 25 °C; catalyst weight: 20 mg; reaction time: 60 min; atmosphere: O_2.

Sample	Chemicals			Crystallite size (nm)	H_2O_2 concentration (mmol L^{-1})	H_2O_2 production rate (mmol g^{-1} h^{-1})
	$ZnSO_4$ ·7H_2O(g)	Se (g)	KBH_4 (g)			
ZS1K1		0.16	0.11		0.019	0.046
ZS1K3		0.16	0.335		0.328	0.820
ZS1.5K3		0.24	0.335		0.364	0.911
ZS1.5K6		0.24	0.67		0.483	1.208
ZS2K3		0.32	0.335		0.301	0.754
ZS2K6		0.32	0.67	13.3	0.604	1.509
ZS2K8		0.32	0.89		0.689	1.722
ZS2K15		0.32	1.65	38.2	0.876	2.189
ZS2K20	0.6	0.32	2.2		1.024	2.560
ZS2K40		0.32	4.4	41.3	1.209	3.023
ZS3K6		0.4	0.67	13.2	0.488	1.219
ZS3K8		0.4	0.89		0.491	1.227
ZS3K15		0.4	1.65		1.016	2.540
ZS3K20		0.4	2.2		1.207	3.017
ZS3K40		0.4	4.4	42.1	1.498	3.745
ZS4K8		0.56	0.89		0.632	1.579
ZS4K40		0.56	4.4	45.8	1.610	4.025
ZS6K40		0.88	4.4		1.010	2.525
ZS8K40		1.2	4.4	37.4	1.261	3.153

Table S2. The AQY values with different incident light wavelengths. Reaction conditions: V_{H2O} = 45 mL, V_{IPA} = 5 mL; light intensity: 10 mW·cm^{-2}; temperature: 25 °C; catalyst weight: 20 mg; reaction time: 60 min; atmosphere: O_2.

Wavelength (nm)	**H_2O_2** Concentration (mmol·L^{-1})	**H_2O_2 production rate (mmol g^{-1} h^{-1})**	AQY (%)
365	0.447176±0.041	1.11794±0.102	5.764±0.528
420	0.253234±0.01	0.633085±0.025	2.837±0.410
485	0.226504±0.01	0.56626±0.02	2.197±0.481
535	0.0945±0.052	0.23625±0.129	0.831±0.214
585	0.0750275±0.005	0.18756875±0.012	0.603±0.114
630	0.048034±0.002	0.120085±0.006	0.359±0.159

2. Supplementary Figures

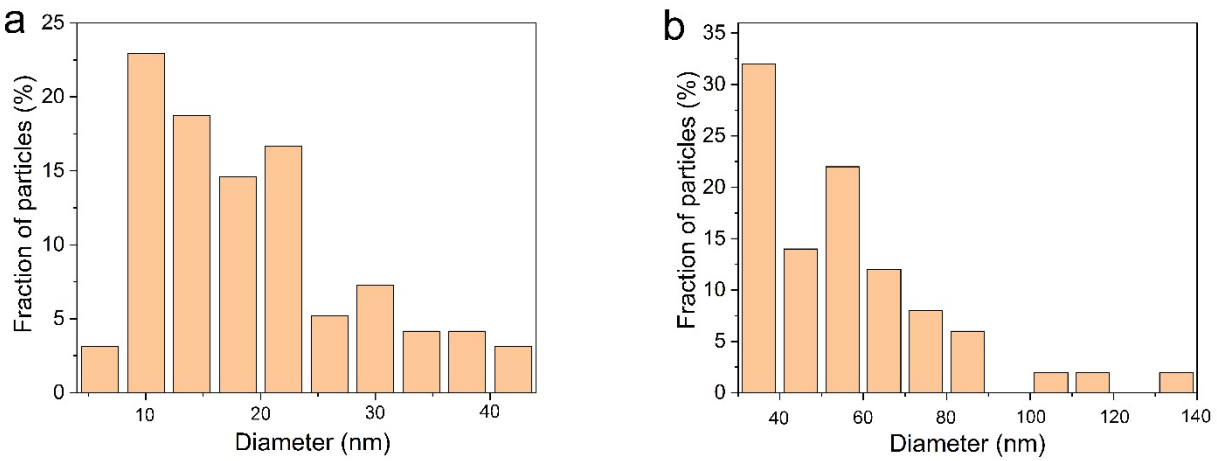

Fig. S1. Histograms demonstrating size distribution of (a) ZS3K6 and (b) ZS4K40 obtained through analysis of sizing based on TEM images.

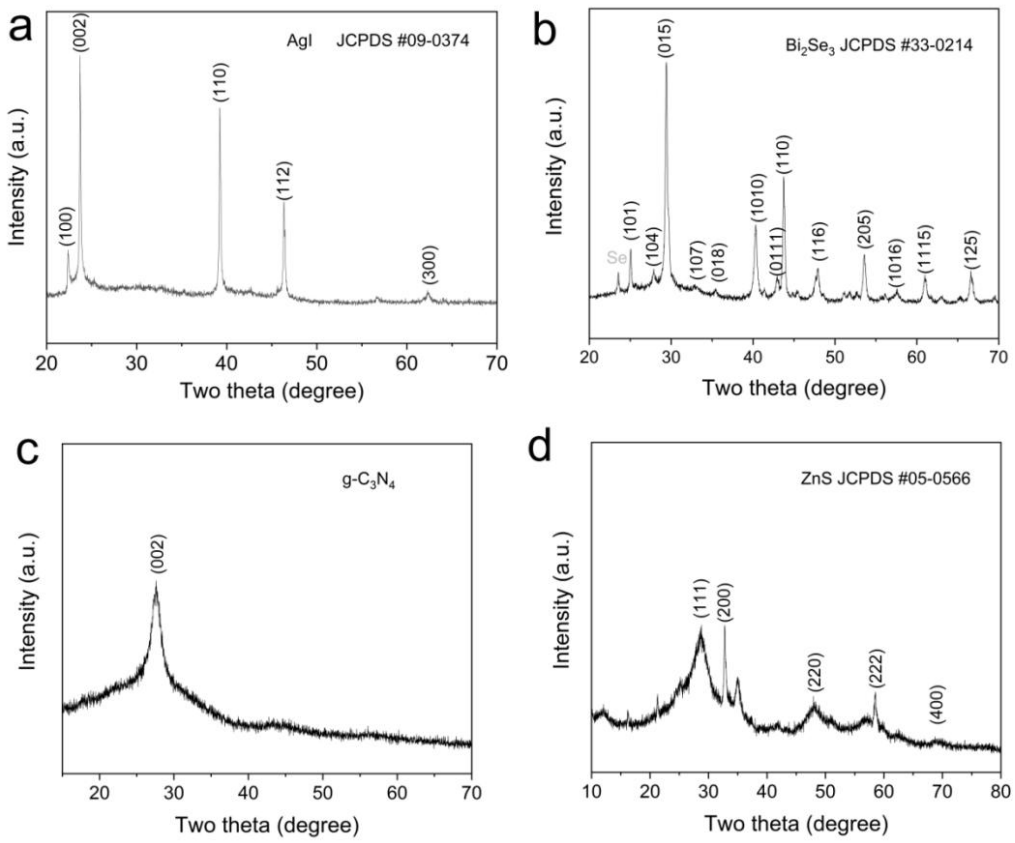

Fig. S2. XRD patterns of the as-prepared (a) AgI, (b) Bi_2Se_3, (c) g-C_3N_4 and (d) ZnS.

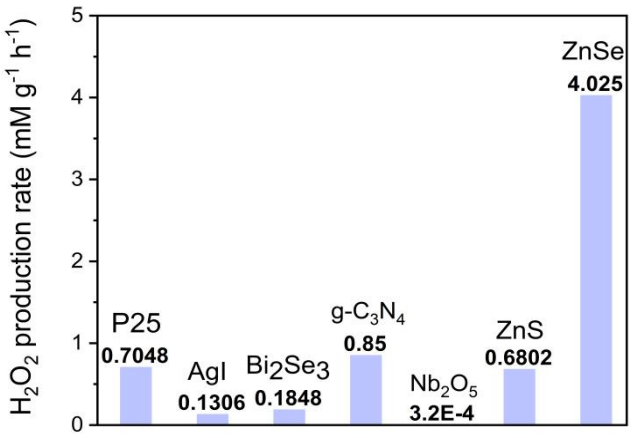

Fig. S3. Photocatalytic H_2O_2 production over P25, AgI, ZnS, Bi_2Se_3, g-C_3N_4 and Nb_2O_5 under simulated sunlight irradiation. Reaction solution: V_{H2O} = 45 mL, V_{IPA} = 5 mL; light intensity: 100 mW·cm^{-2}; catalyst weight: 20 mg; reaction time: 60 min; atmosphere: O_2.

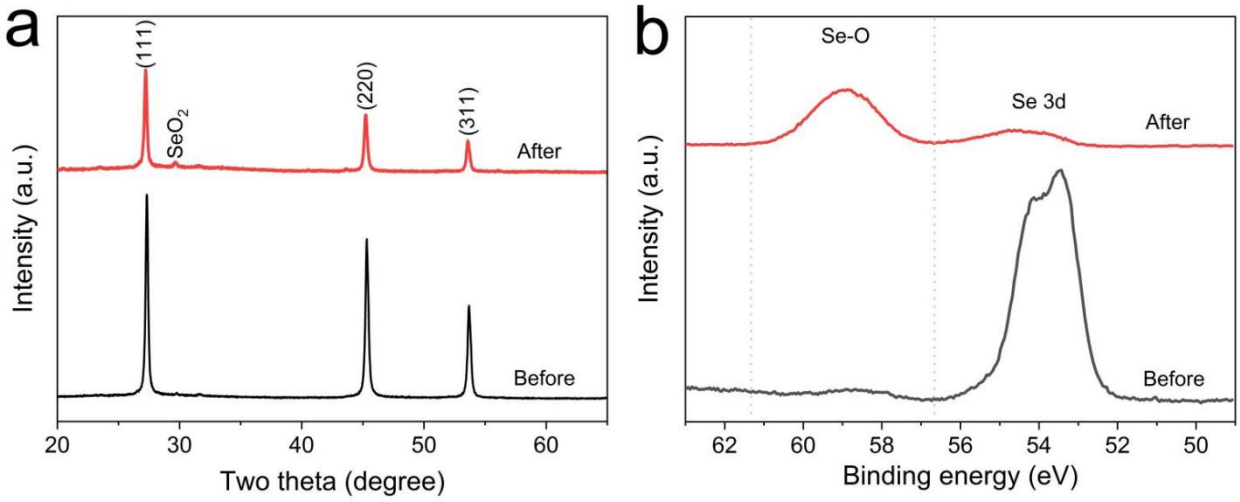

Fig. S4. (a) XRD patterns and (b) high resolution Se 3d XPS spectra of the fresh and used ZS4K40 samples.

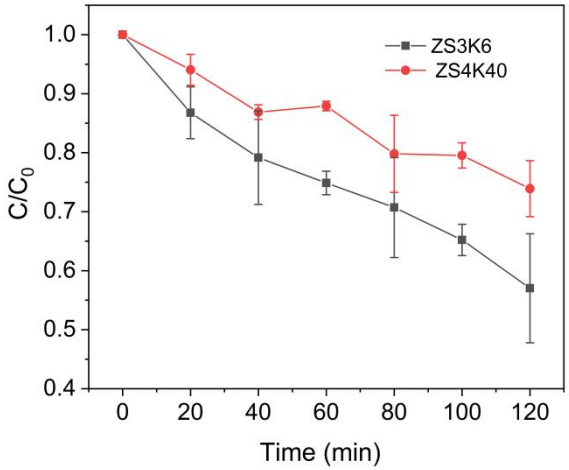

Fig. S5. Time-dependent curves of photocatalytic H_2O_2 decomposition over ZS3K6 and ZS4K40. Reaction solution: V_{H2O} = 50 mL; light intensity: 100 mW·cm^{-2}; catalyst weight: 20 mg; reaction time: 120 min;

atmosphere: N_2.

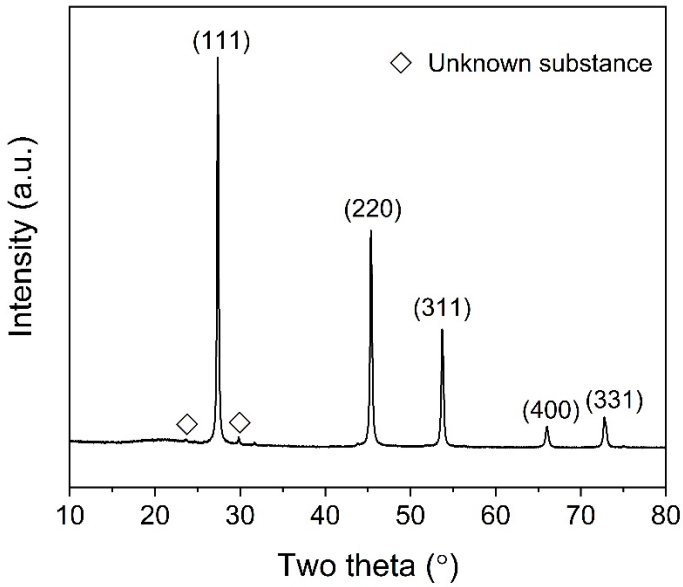

Fig. S6. The XRD result of the H_2O_2 treated ZnSe nanocrystals (ZS4K40). Reaction condition: 0.1 g ZnSe nanocrystals was added into 200 mL of 2 mmol L^{-1} H_2O_2 solution and kept at room temperature for 48 h.

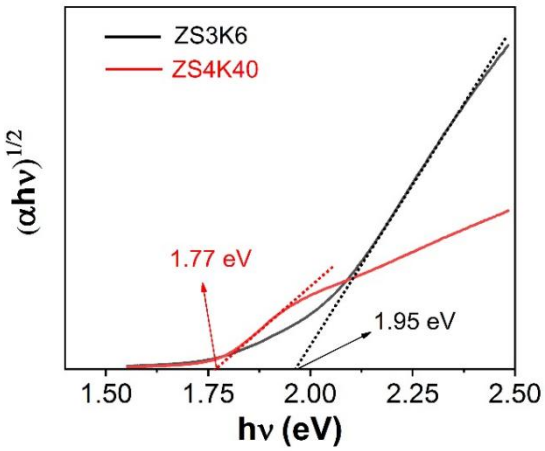

Fig. S7. Kubelka-Munk plots converted from the UV–vis spectra of ZS3K6 and ZS4K40.

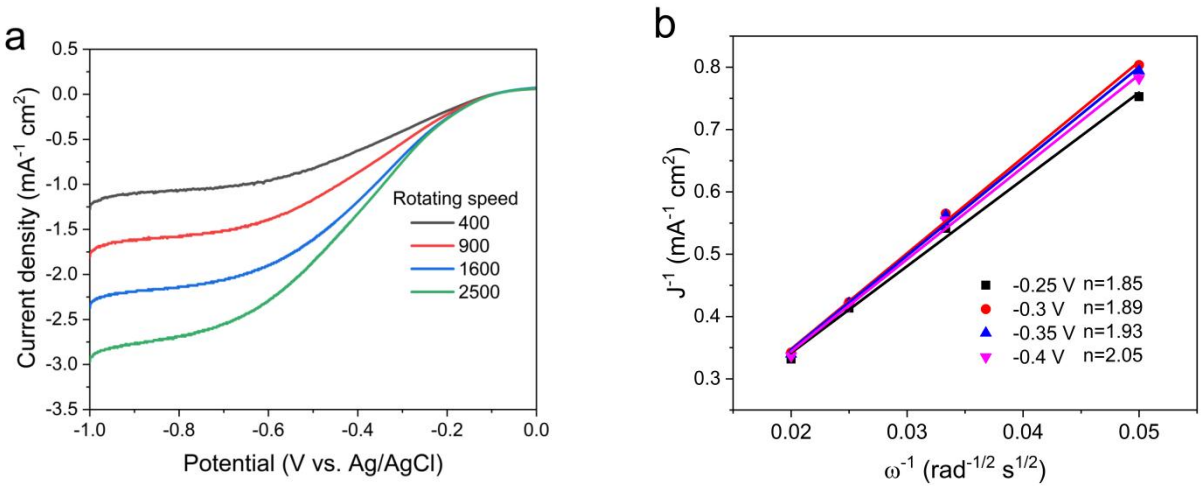

Fig. S8. (a) LSV curves of ZS3K6 measured on RDE at different rotating speeds. (b) Koutecky-Levich plots of ZS3K6 at different potentials, evaluating the number of electrons participating in the ORR.

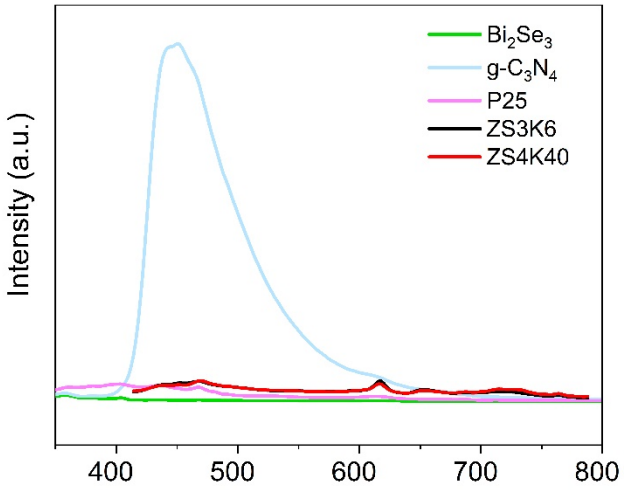

Fig. S9. The PL spectra of Bi_2Se_3, P25, g-C_3N_4, ZK3S6 and ZK4S40.

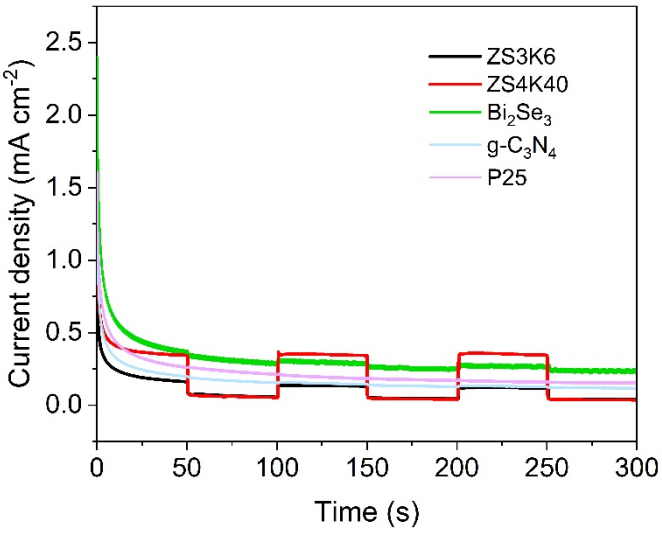

Fig. S10. The transient photocurrent response of Bi_2Se_3, P25, g-C_3N_4, ZK3S6 and ZK4S40.

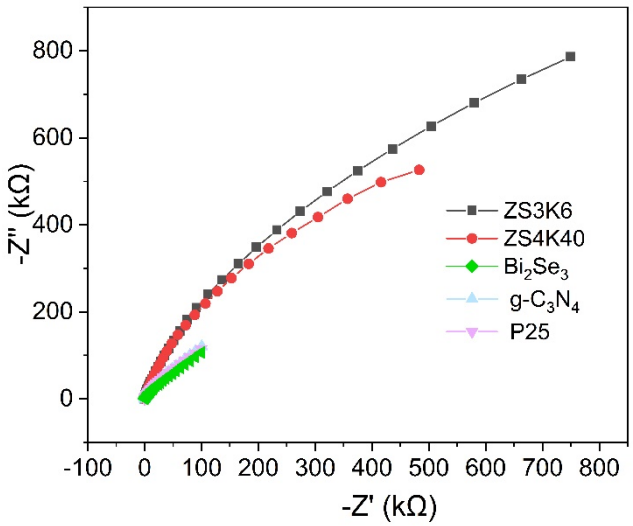

Fig. S11. The EIS Nyquist plots of Bi_2Se_3, P25, g-C_3N_4, ZK3S6 and ZK4S40.

The PL, transient photocurrent response and EIS Nyquist plots of P25, Bi_2Se_3 and g-C_3N_4 were tested and compared with ZK3S6 and ZK4S40, as shown in the below pictures of Fig. S6-S8. However, there is no reasonable results can be used to explain the advanced performance of ZnSe for H_2O_2 production, probably because P25, Bi_2Se_3 and g-C_3N_4 are quite different semiconductors compared with ZnSe. According to most of the previous reports, these methods are more prone to compare the analogous materials, such as the pristine semiconductors and their doped derivatives, heterojunctions with varied content of two semiconductors. It is difficult to evaluate the photocatalytic performance of different semiconductors just through the charge carrier transfer ability. Some other factors maybe play an important role, such as crystallinity, band alignment, and so on. For example, the PL emission intensity of g-C_3N_4 is significantly higher than P25 and Bi_2Se_3, indicating its higher rate of electron-hole recombination. However, g-C_3N_4 shows better ability for H_2O_2 production. Similar results are also observed in the transient photocurrent response and EIS Nyquist plots.

References

[1] P. Zhang, C. Peng, H. Li, J. Huang, Y. Wang, Y.Q. Yu, S.M. Ding, S. L. Liu, Y.C. Zhao, Wavelength-dependent generation of reactive species in the photodegradation process over pure and C-doped Nb_2O_5, Sep. Purif. Technol. 286 (**2022**)120406.

[2] Y. Zhao, Y. Liu, J. Cao, H. Wang, M. Shao, H.Huang, Y.Liu, Z. Kang, Efficient production of H_2O_2 via two-channel pathway over ZIF-8/C_3N_4 composite photocatalyst without any sacrificial agent, Appl. Catal. B-Environ. 278 (**2020**)119289.