Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Three-Dimensional Heterostructured ZnSe NPs/Si Wires Arrays with Enhanced Photocurrent and Photocatalytic Performances

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Supporting Information

The diameter and length of SiWs were measured from SEM images. As shown in Figure 1(f), the SiWs are fairly uniform in length and diameter. Figure S1a, b show diameter and length distribution of SiWs, respectively. The average diameter is 0.345 μm (deviation：0.014) and mean length is 3.005 μm (deviation：0.108).

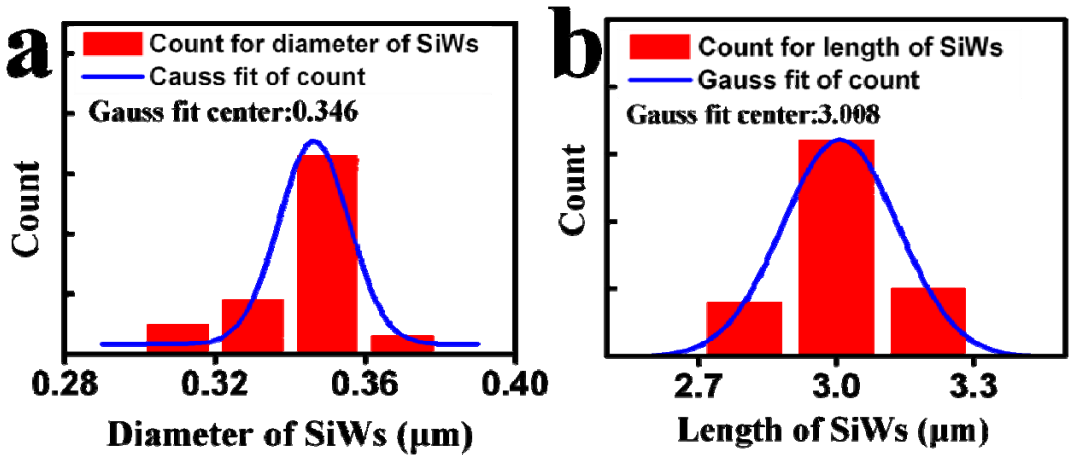

Figure S1. The distribution of (a) diameter and (b) length of SiWs.

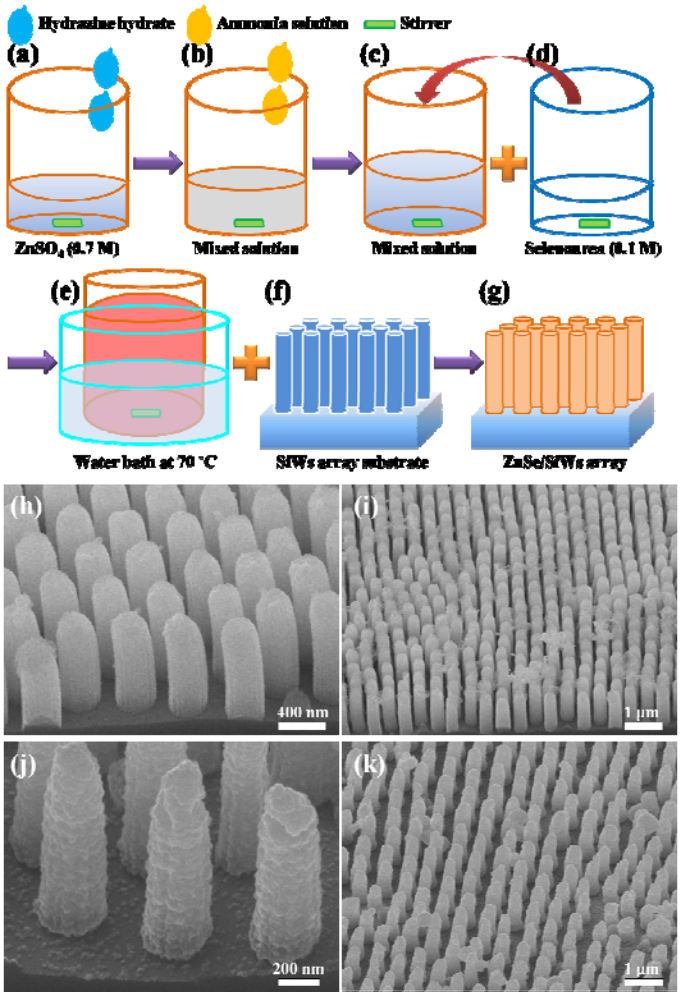

Figure S2. The schematic plot of the fabrication process of three-dimensional heterostructured ZnSe NPs/SiWs arrays with the SEM images of large-scale SiWs and ZnSe NPs/SiWs arrays at different magnifications. Initially hydrazine hydrate solutions are added to 0.7M $ZnSO_4$ (**Figure (a)**). Then, ammonia solution is added which will turn the milky cream solution to a limpid solution (**Figure S2 (b)-(c)**). This is followed by adding 0.1M selenourea solution as shown in the **Figure S2 (d)**. The SiWs substrates are then placed in the solution and water bath reaction is carried out at 70℃ (**Figure S2 (e)-(f)**). The ZnSe NPs/SiWs array was taken out of the beaker (**Figure S2 (g)**). The cross-section SEM images in **Figure S2 (h) and (i)** reveal the large-area SiWs arrays. **Figure S2 (j) and (k)** are images of heterostructured ZnSe NPs/SiWs arrays coated with ZnSe NPs on the SiWs exhibiting rough surfaces.

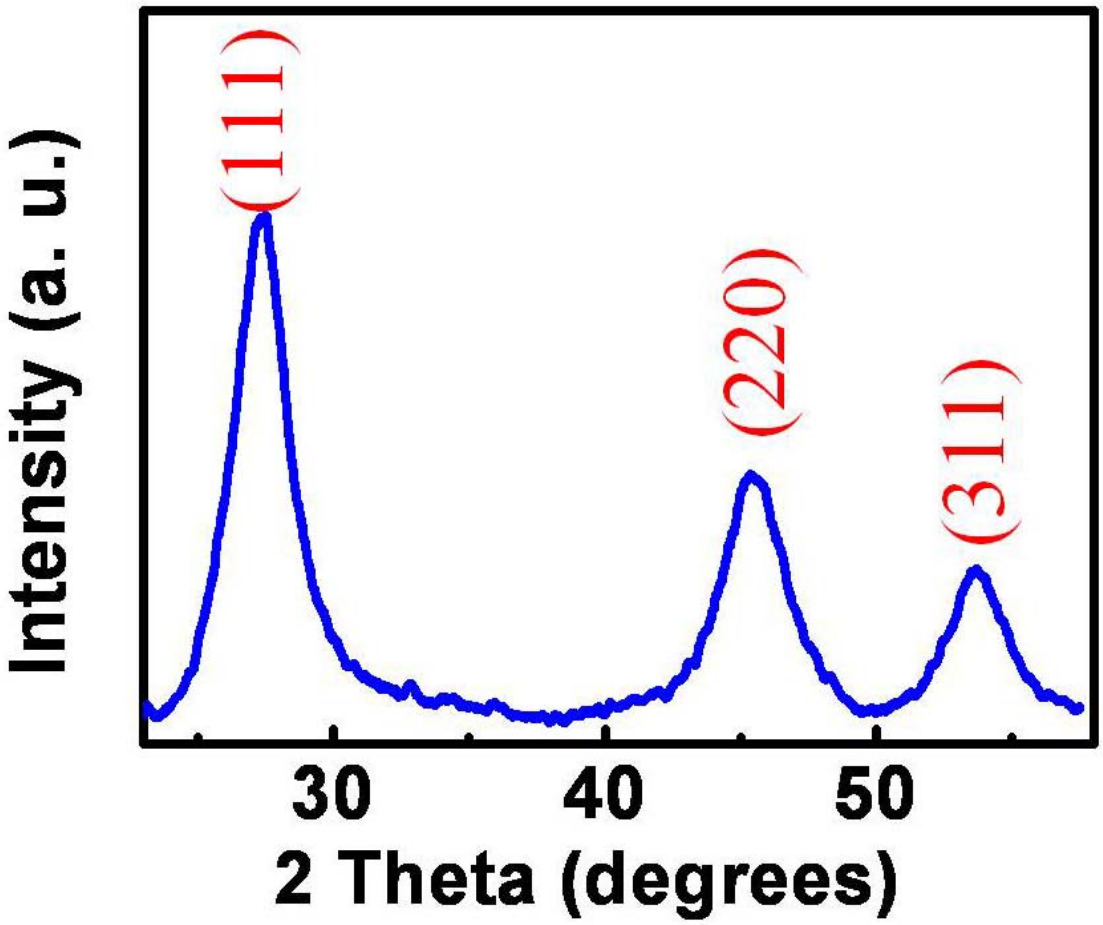

Figure S3. XRD spectrum of precipitated NPs of ZnSe.

The broadening of diffraction peaks is attributed to the small crystallite size. According to Scherrer's equation [41]

$$t = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

where t is the diameter of the particle, K is the shape factor that was taken to be equal to 0.9, λ is the wavelength of the X-ray, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg angle of the diffraction peak. The average size of ZnSe NPs is estimated to be about 4 nm.

$t_{(111)}=0.9\times0.154/(0.039599\times0.888728)=3.938$

Table S1. The XRD data and results for three peaks are listed below.

Peak	(111)	(220)	(311)
θ, diffraction peak	27.3°	45.4°	53.6°
cosθ	0.888728	0.791978	0.935022
β, full width at half maximum (FWHM)	2.27°	2.73°	2.5°
β, angle in radians	0.039599	0.047623	0.043611
t, diameter of the particle (nm)	3.938	4.143	5.352

We choose the (111), (220) peaks for the calculation. The average size of NPs is 4.04 nm. As the size of ZnSe NPs is rather small, the Scherrer equation can adequately determine the average size of crystallites.

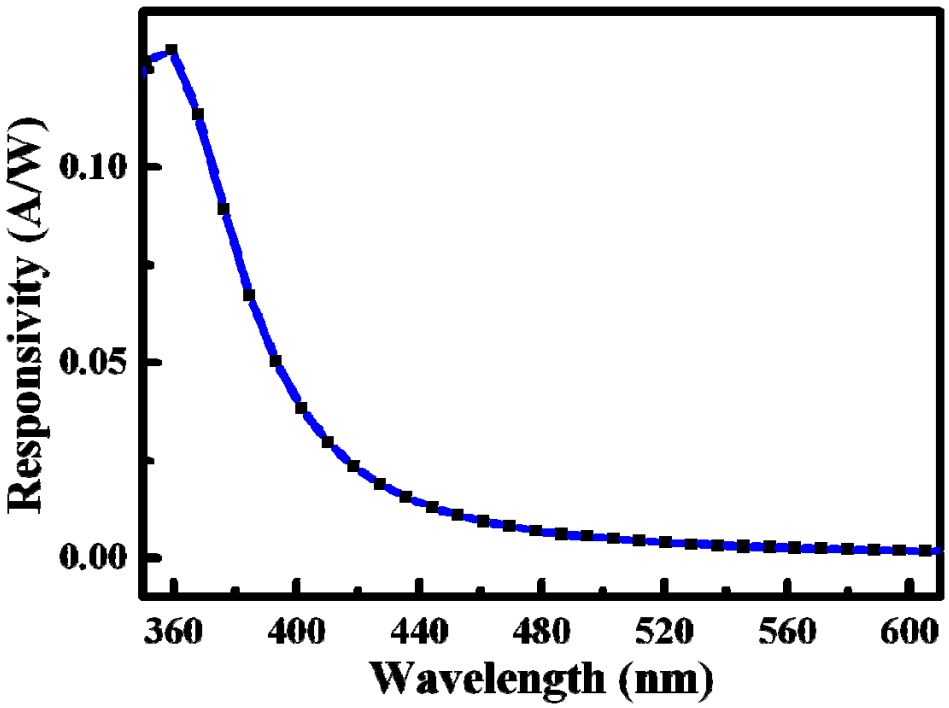

Figure S4. The responsivity measured with a bias of 1.5 V at 350–600nm wavelengths.

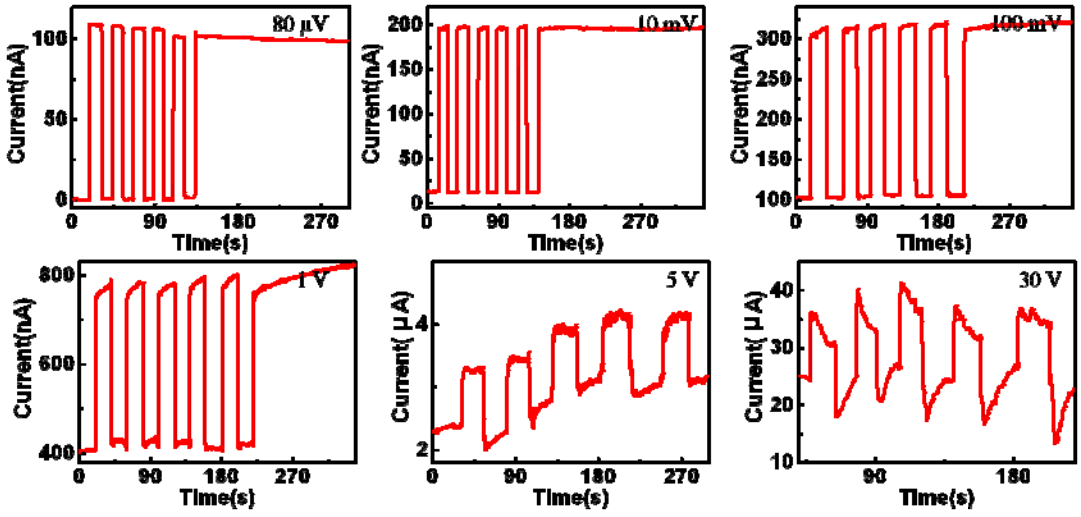

Figure S5. The photoresponse curves for different applied bias voltages.

Table S2. The summary of the photoconductive performance of the ZnSe NPs/Si MWs arrays.

Voltage	Dark current (nA)	Photo current (nA)	Immediate decay %	On/off ratio	Response time (s)	ΔI (I_{UV}-I_{dark}) (nA)
80 μV	0.15	109	99.85	725.67	<0.4	108.85
10 mV	13.3	197	93.57	13.81	<0.4	183.7
100 mV	104	311	65.71	1.99	<0.5	207
1 V	409	791	46.52	0.93	<0.5	382
5 V	2850	3430	29.02	0.20	<2.3	580
30 V	25100	40200	35.02	0.60	<2.2	15100

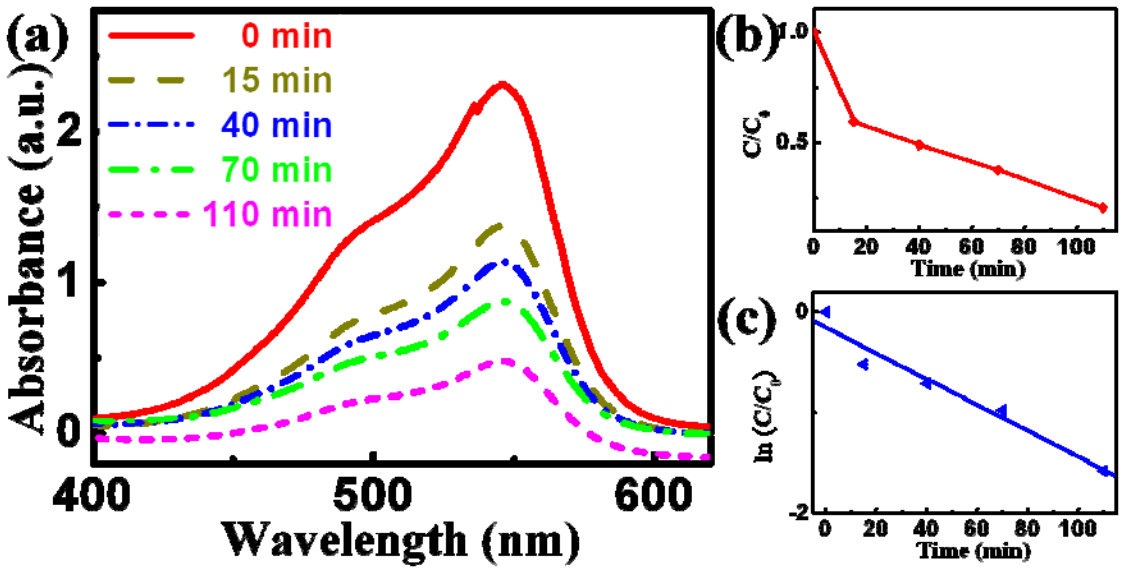

Figure S6. (a) UV-Vis spectra (b) C/C_0 and (c) ln C/C_0 v.s. time curves of the photodegradation of AF by ZnSe NPs/SiWs array.

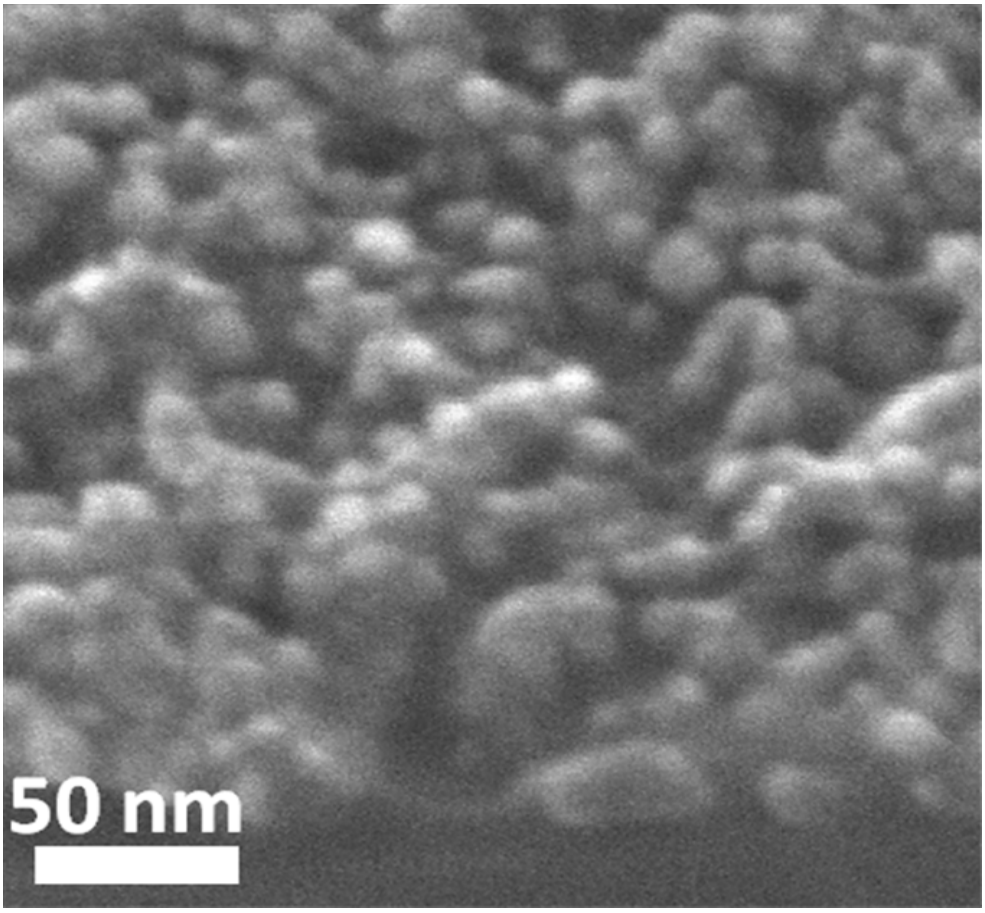

Figure S7. Tiled-view SEM image of ZnSe NPs film on Si wafer which is used in photodegradation reaction. The samples of ZnSe film/Si wafer were prepared by coating ZnSe NPs on Si wafer with the same time as the coating of ZnSe NPs on SiWs. The film thickness of ZnSe NPs was estimated to be 10~30 nm.

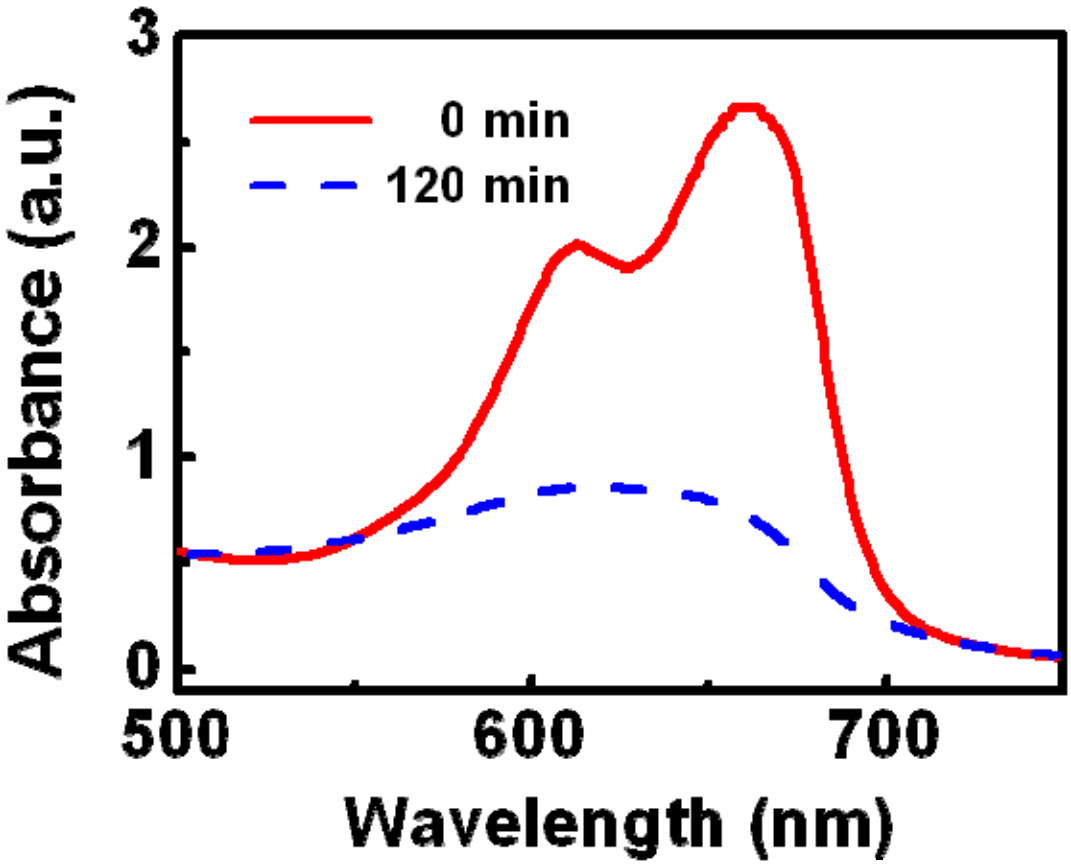

Figure S8. The UV-Vis spectra of the photodegradation of MB by P25 TiO_2.