Two dimensional $NbSe_2/Nb_2O_5$ metal-semiconductor heterostructure based photoelectrochemical photodetector with fast response and high flexibility

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1. scanning electron microscopy (SEM)

To clearly observe the microstructure $NbSe_2/Nb_2O_5$ film, scanning electron microscopy (SEM) was conducted as shown in Figure S1. The results show that the nanosheets were successfully deposited onto substrate to form a uniform $NbSe_2/Nb_2O_5$ films as shown in Figure S1(a). The nanosheet size is approximately 113 nm in length and from 90 nm in width (in Figure S1(b-c)), in line with TEM results in Figure 2. The sectional-view morphology was also measured and the thickness of $NbSe_2/Nb_2O_5$ film is approximately 367.76 nm as shown Figure S1(d).

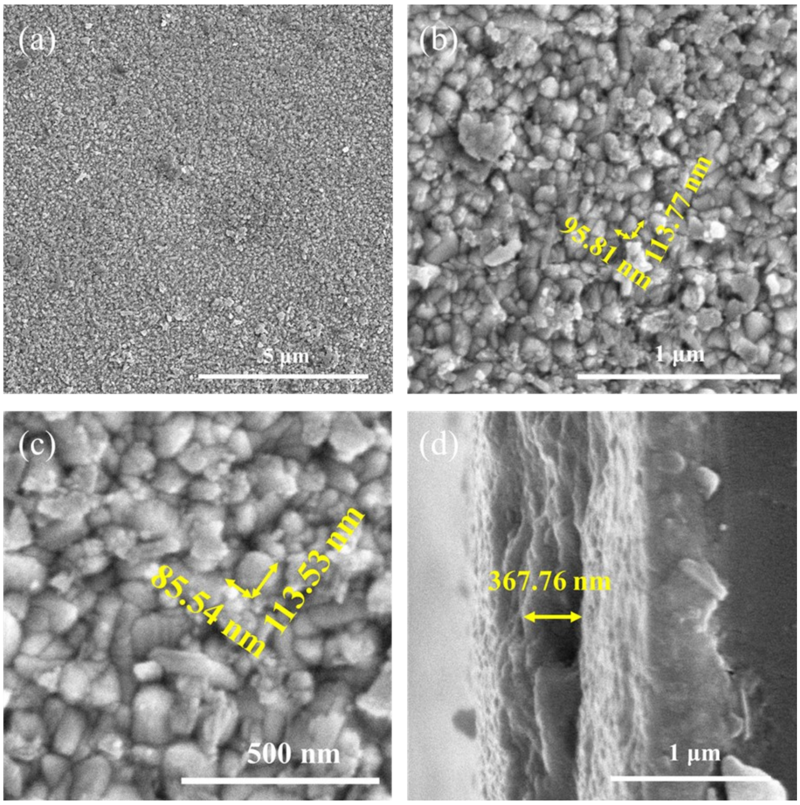

Fig. S1 (a-c) Top SEM images and (d) sectional-view SEM image of $NbSe_2/Nb_2O_5$ metal-semiconductor heterostructure.

2. X-ray diffraction and UV-Vis absorption spectrum

To verify the sample overall composition and crystalline structure, X-ray diffraction (XRD) measurement was performed (Fig. S2a). The bulk powder and exfoliated nanosheets of $NbSe_2$ were characterized and two obvious peaks at 14.26 and 43.49^o correspond to (0 0 4) and (0 0 6) planes, indicating the successful preparation of $NbSe_2$ nanosheets[1]. Besides, several peaks at 37.29, 42.03, 53.44, and 59.14^o corresponding to (1 0 3), (1 0 4), (1 0 6), and (0 0 8) plane also suggest the polycrystalline of $NbSe_2$ powder. However, other peaks at 9.66, 47.59, and 60.5^o from Nb_2O_5 indicate the presence of surface oxidation due to moisture sensitivity. Furthermore, the $NbSe_2/Nb_2O_5$ shows a high light absorption and broad band absorption from 400 to 900 nm (Fig. S2b).

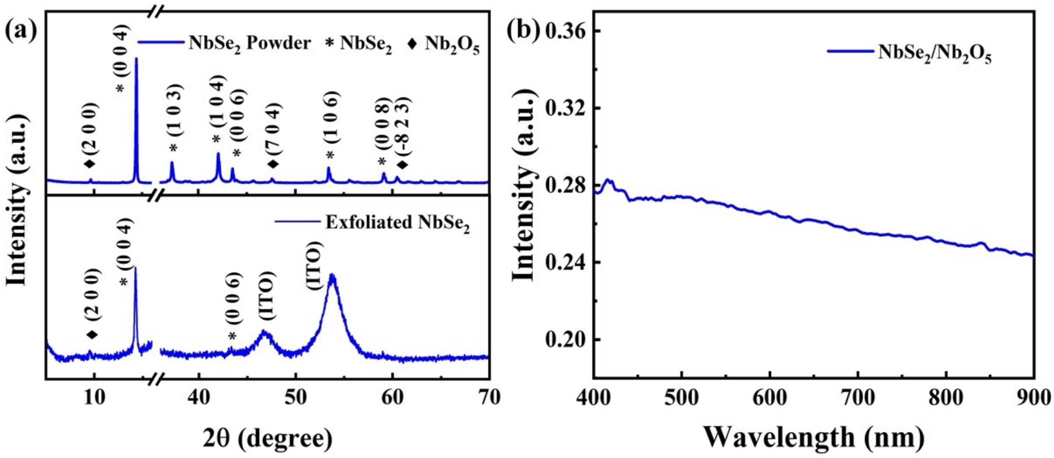

Fig. S2 (a) XRD pattern, and (b) UV-Vis absorption spectrum.

3. Photoelectric measurement of 2D $NbSe_2/Nb_2O_5$

The photoelectric properties were measured under the simulated sunlight illumination at 100 mW/cm^2 and the I-V curve shows an evident photovoltaic activity (Fig. S3a). The results show the photodetectors are sensitive to the external bias voltage. Firstly, time-dependent photocurrent density of the $NbSe_2/Nb_2O_5$-5000 photodetector was measured without external voltage (Fig. S3b). There is an evident on/off I-t signal and the photocurrent density (I_{ph}) is approximately 0.55 μA/cm^2. Accordingly, the calculated R_{ph} is 5.54 μA/W (Fig. 5d).

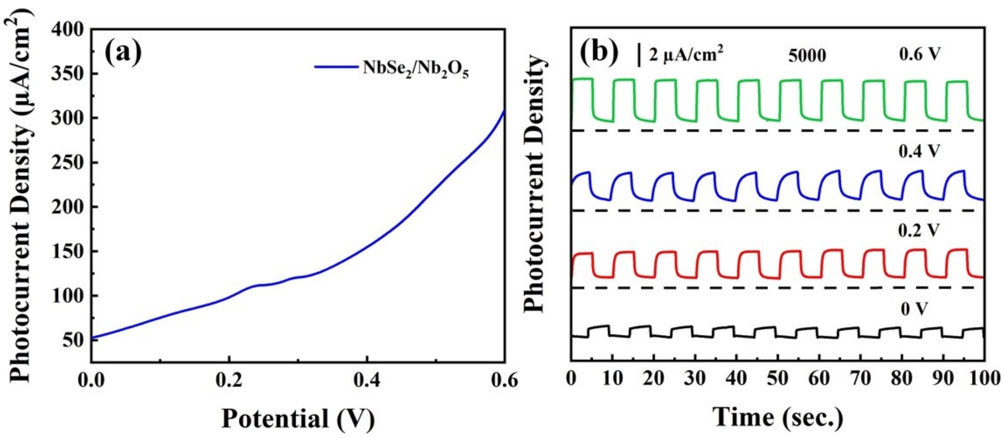

Fig. S3 (a) I-V curve from 0 to 0.6 V; (b) time-dependent photocurrent density under different applied voltage.

4. Schematic of charge transfer mechanism of $NbSe_2/Nb_2O_5$

The charge transfer process of $NbSe_2/Nb_2O_5$ under light irradiation has been illustrated as shown in Figure S4 in this response letter. When the Nb_2O_5 metal-semiconductor heterostructure is illuminated, the carrier quickly separates and the electrons enter conduction band. Due to the excellent electrical conductivity and electronic transport capability, the photogenerated electrons of Nb_2O_5 were quickly transferred toward $NbSe_2$. Subsequently, more photogenerated electrons of $NbSe_2/Nb_2O_5$ heterostructure are collected at the flexible ITO-coated PET substrate and then migrated into the counter electrode, resulting in a stronger electrical signal and improving optical detection performance.

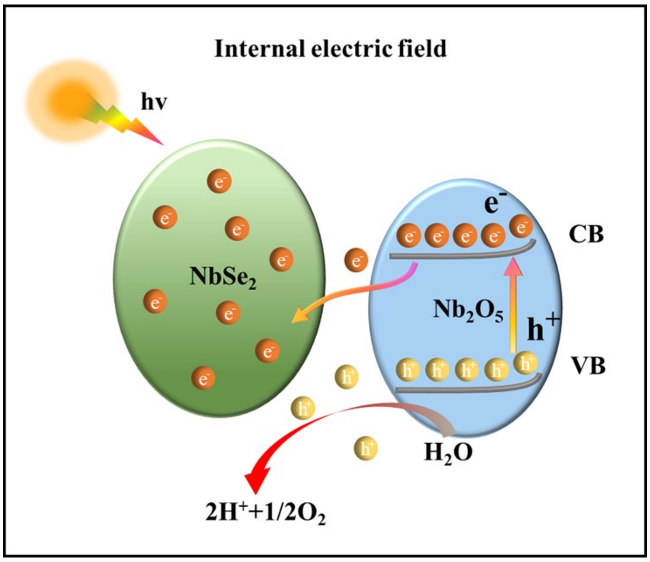

Fig. S4 Schematic of charge transfer mechanism of NbSe2/Nb2O5 under light irradiation

Table S1 PEC activity comparison of $NbSe_2/Nb_2O_5$ nanosheets under the different measurement conditions

Materials	Measurement conditions	Sample	I_{ph}	R_{ph}
$NbSe_2/Nb_2O_5$	1 M Na_2SO_4 0.2 V	1000	0.25 μA/cm^2	2.52 μA/W
		3000	1.63 μA/cm^2	16.25 μA/W
		5000	1.69 μA/cm^2	16.95 μA/W
		7000	0.31 μA/cm^2	3.06 μA/W
	1 M Na_2SO_4 0.4 V	1000	0.73 μA/cm^2	7.30 μA/W
		3000	1.38 μA/cm^2	13.83 μA/W
		5000	1.46 μA/cm^2	14.62 μA/W
		7000	0.79 μA/cm^2	7.94 μA/W
	1 M Na_2SO_4 0.6 V	1000	1.75 μA/cm^2	17.47 μA/W
		3000	2.21 μA/cm^2	22.07 μA/W
		5000	2.32 μA/cm^2	23.21 μA/W
		7000	1.88 μA/cm^2	18.80 μA/W

5. X-ray photoelectron spectroscopy (XPS) characterization

To characterize the surface oxidization after the measurement, XPS was used (Fig. S5a-c). The Se 3d spectrum from $NbSe_2$ is fitted by Se $3d_{5/2}$ (53.5 and 54.8 eV) and Se $3d_{3/2}$ (55.3 eV). It is evident that the $NbSe_2$ decreases while the SeO_2 increase (Fig. S5 a). Furthermore, the fitted O and Nb elements further confirm the increased surface oxidation (Fig. S5b-c).

To verify the oxygen adsorption and desorption process, the oxygen purges electrolyte and enables more oxygen into the electrolyte. The XPS results (Fig. S5d-f) confirm that the surface layer of $NbSe_2$ has been fully oxidized and the oxygen is enough.

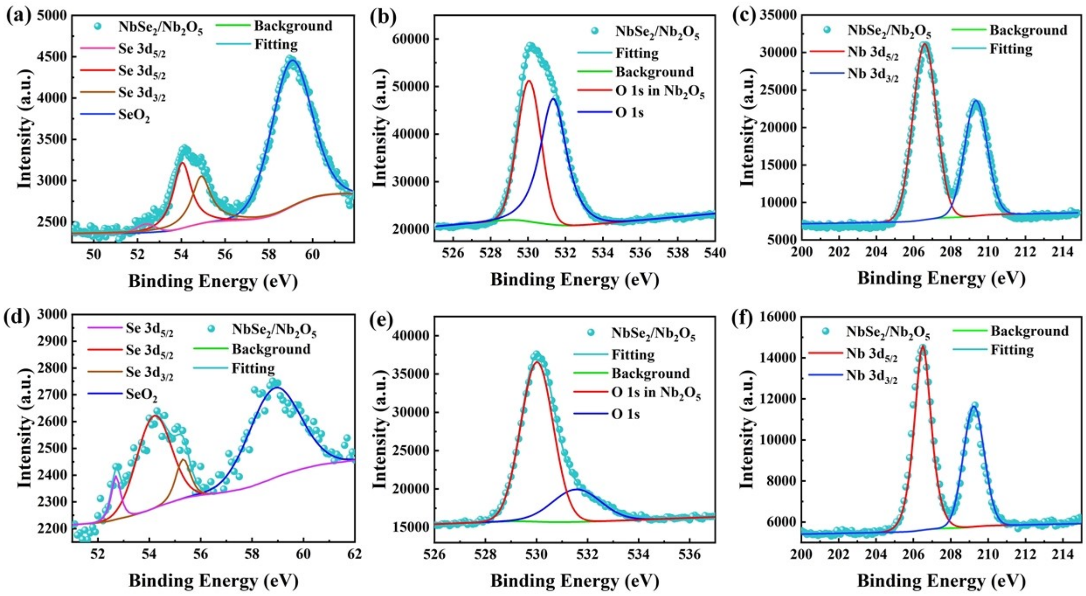

Fig. S5 XPS signal of $NbSe_2/Nb_2O_5$ with (a) Se, (b) O, and (c) Nb elements after the measurement; XPS signal of $NbSe_2/Nb_2O_5$ nanosheets with (d) Se, (e) O, and (f) Nb elements in enough oxygen condition.

6. Photos of the photodetectors under 0, 100, 200, and 300 cycles

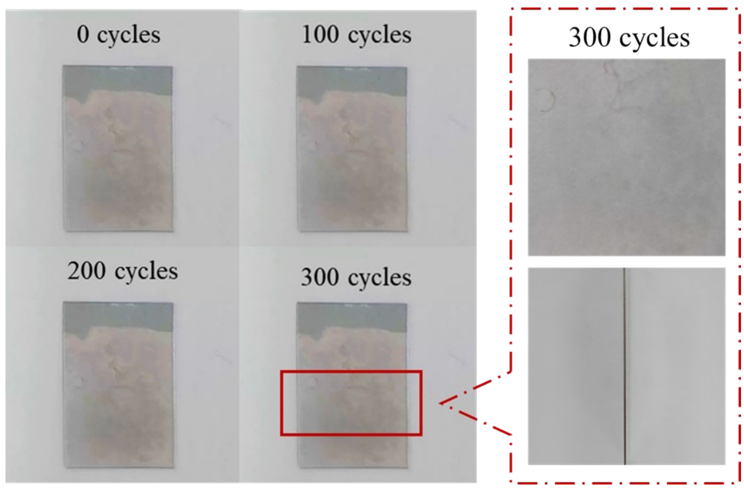

Fig. S6 Photos of the photodetectors under 0, 100, 200, and 300 cycles

Reference:

1 N. D. Boscher, C. J. Carmalt and I. P. Parkin, *European Journal of Inorganic Chemistry*, 2006, **2006**, 1255-1259.