Section I: band structures and density of states of the B2X3 (X= S, Se)

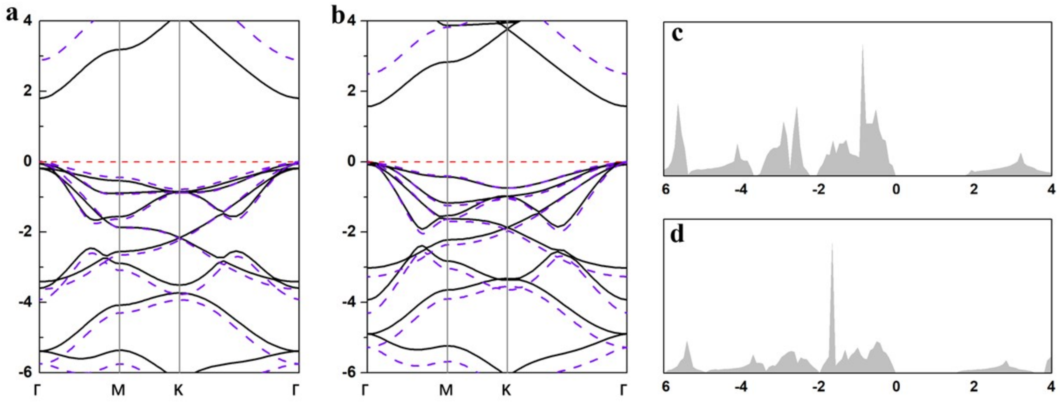


Figure S1. The band structures and the total density of states for B_2S_3 and B_2Se_3 respectively. (a) and (c) are B2S3; b and d are B2Se3. In band structures black lines are for PBE calculation, the purples dash lines are for HSE06 calculations.

Section II: Detailed TMD analysis

According to the detailed group analysis at Γ point (in symmetry of D_{3h}), the generated VBM belongs to the two-fold generated E', which is totally different from CBM (A''_1). However, the other VB belongs to the two-fold generated E'', which consists two bands and reduce the symmetry into A'', which is in the same parity with CBM, this would produce a robust platform for photon exciting. With ***k*** moving in the BZ, the symmetry reduces into C_s, the two generated VBs degenerated into four VBs namely, VBM-1, VBM-2, VBM-3, and VBM-4. VBM-1 and VBM-2 keep the transition forbidden around Γ point. The other two bands maintain the same symmetry as the CB shown in Figure S2 (a) and (c). After a series of band crossing and rearrangement, our defined VBM-3 becomes the energy-highest VB, and maintains the symmetry, which would produce a platform for photon excitation. We calculated the TDM of B_2X_3 (B_2Te_3 as an example shown in Figure 4a). The TDM agrees well with the symmetry analysis above (Γ to M is considered only since the band structures are too complex and mix together in other paths). The VBM-1 and VBM-2 contribute no value of TDM at Γ point, however, VBM-3 and VBM-4 possess a TDM peak due to the symmetry. With the wave vector ***k*** moving at the path Γ to M, the tendency of the value of TDM is completely consistent with the symmetry analysis (shown in Figure 4a). With the giant contribution from VBM-3 and VBM-4, B_2Te_3 is calculated a light absorption peak around band gap (shown in figure 4b), which endows it an application for visible light photo-catalysis.

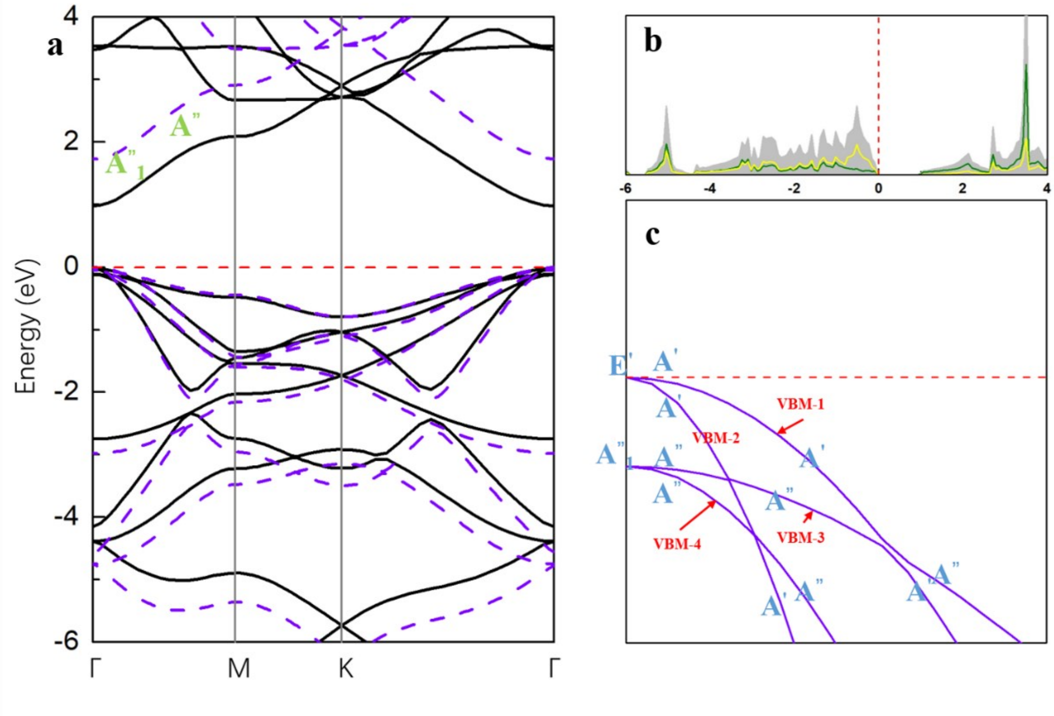


Figure S2. The electronic properties of B_2Te_3. (a) the band structure of B_2Te_3 calculated by PBE and HSE 06 (purple dashed lines) respectively; (b) the calculated density of states of B_2Te_3 via PBE. The green and the yellow line represents the contribution of B and Te atoms. The gray background represents the total DoS of B_2Te_3. The VBs near Fermi level and CBM are distributed from different atoms, which means the transition between these states are dipole-allowed according to the selection rule; (c) the detailed band structure and irreducible representation of the four valence bands at the path of Γ to M. With k moving in the Brillouin zoon and the band crossing, the band may be rearranged according to the energy. We define these four bands with the order.

From the partial charge analysis (Figure S3) and projected DoS (Figure S2b), we can also know that every VB mostly distributed from the different atoms (orbitals) from CB (B and S respectively), which follows the selection rule partly. Thus, the transition between the VBs and CBM states at Γ point can be easy induced by a photon of ~1.7eV.

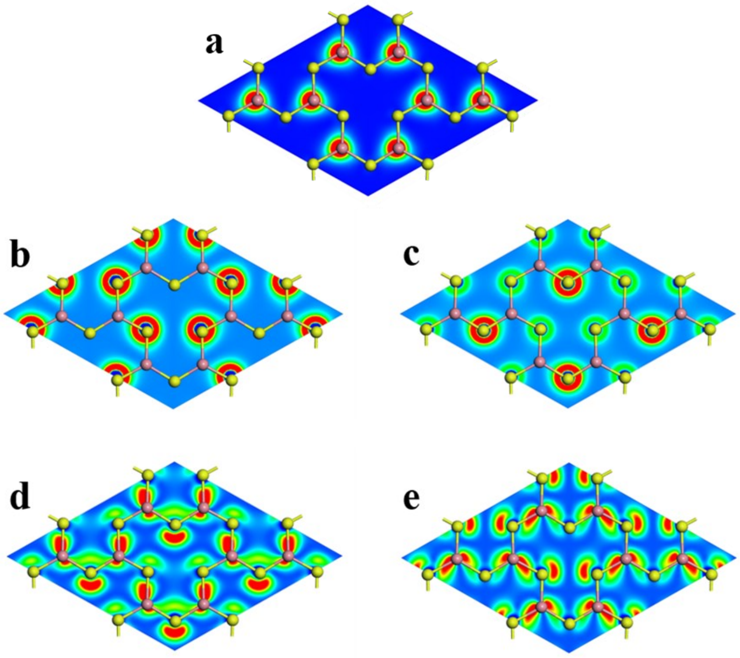


Figure S3. The selection rule of electrons excited. (a)-(e) charge density projected on B_2X_3 of CB and four VBs near Fermi level. We can see that the CB is mainly distributed from the pz orbital of two B atoms from (a). (b) and (c) are the charge density of the VBM-4 and VBM-3 respectively, from which we can see that two bands are mainly distributed from the p_z orbital of chalcogen atoms. According to the selection rule, the transition between CB and these two bands is allowed. (d) and (e) present the VBM-2 and VBM-1, these two bands mainly come from the σ hybridization (s and px/py), which hardly follows the selection rule for photon excited.

Section III: Phonon spectrum of B2Se3

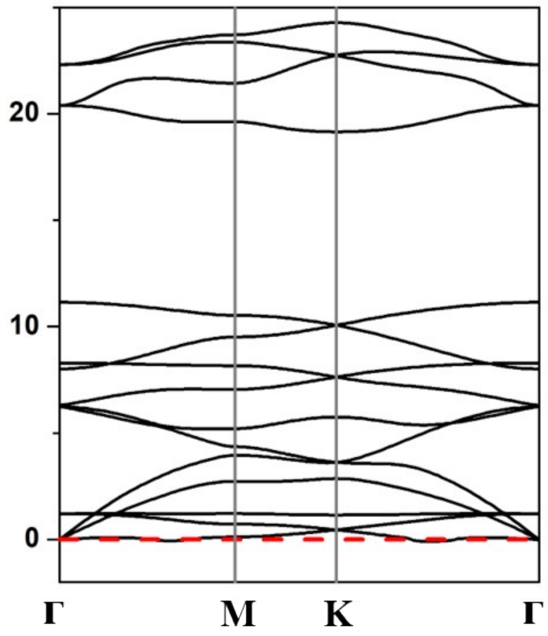
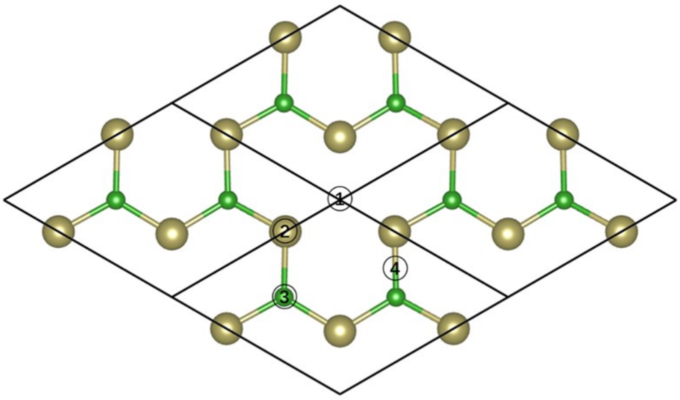


Figure S4 Phonon spectrum for B2Se3. No imaginary part is found in the figure.

Section IV: absorption spot of the nanosheets



	E(eV)–H@B_2Te_3	E(eV)–O@B_2Se_3
1	1.60	4.41
2	4.97	15.43
3	0	0
4	1.18	2.01

Section V: detailed pathway of photocatalyst

Table S1. The Gibbs free energy (G) of molecules and adsorbates in this study.

	G		G
H_2	-6.91	**OOH***	-109.43
H_2O	-14.33	**H***	-85.68
O_2	-10.31	**O***	-103.84
OH*	-107.43		

There are four four-electron oxidation steps in OER process, namely:

$$H_2O + * \rightarrow OH^* + H^+ + e^-$$

$$OH^* \rightarrow O^* + H^+ + e^-$$

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^-$$

$$OOH* \rightarrow * + O_2 + e^-$$

Meanwhile, the HER process with two-electron pathways can be written as:

$$* + H^+ + e^- \rightarrow H^*$$

$$H^* + H^+ + e^- \rightarrow * + H_2$$

Considering the effect of electrode potential (U) and pH, the free energy change can be expressed as:

$$\Delta G_1 = G_{OH^*} + 1/2G_{H_2} - G_{H_2O} - G^* - \Delta G_U - \Delta G_{pH}$$

$$\Delta G_2 = G_{O^*} + 1/2G_{H_2} - G_{OH^*} - \Delta G_U - \Delta G_{pH}$$

$$\Delta G_3 = G_{OOH^*} + 1/2G_{H_2} - G_{H_2O} - G_{O^*} - \Delta G_U - \Delta G_{pH}$$

$$\Delta G_4 = G^* + 1/2G_{H_2} + G_{O_2} - G_{OOH^*} - \Delta G_U - \Delta G_{pH}$$

$$\Delta G_5 = G_{H^*} - 1/2G_{H_2} + G^* - \Delta G_U + \Delta G_{pH}$$

$$\Delta G_6 = G^* + 1/2G_{H_2} - G_{H^*} - \Delta G_U + \Delta G_{pH}$$