Supporting Information：

Computational design of enhanced photocatalytic activity of two-dimensional cadmium iodide

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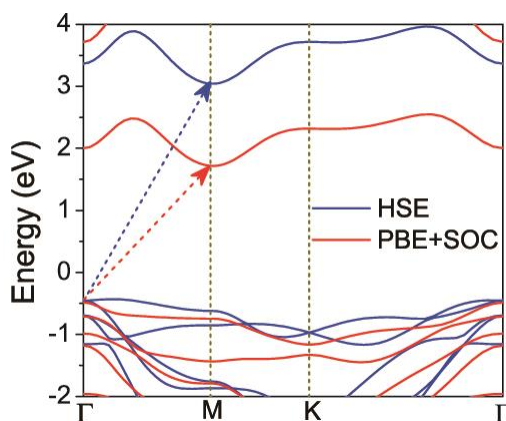
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Figure S1. Band structure of monolayer CdI$_2$ by HSE06 hybrid functional (blue lines) and PBE functional with spin-orbit coupling taken into consideration (red lines).

In Figure S1, the HSE06 hybrid functional is adopted to describe the electron exchange and correlation. Comparing with the band structure of monolayer CdI$_2$ in Figure 1b, the general features of band structure of monolayer CdI$_2$ are well preserved on HSE06 level except for a larger band gap. To take spin-orbit coupling (SOC) effect into consideration, band structure with SOC effect is also calculated in Figure S1 (red lines). An obvious spin-orbit splitting is observed at the valence band maximum (VBM). This is attributed to the strong coupling between Cd_d and I_p orbitals at the VBM. While, the conduction band minimum (CBM) subjects little influence of SOC effect. Absence of Cd_d at the CBM in the band structure of monolayer CdI$_2$ results in the little reponse to the SOC effect.
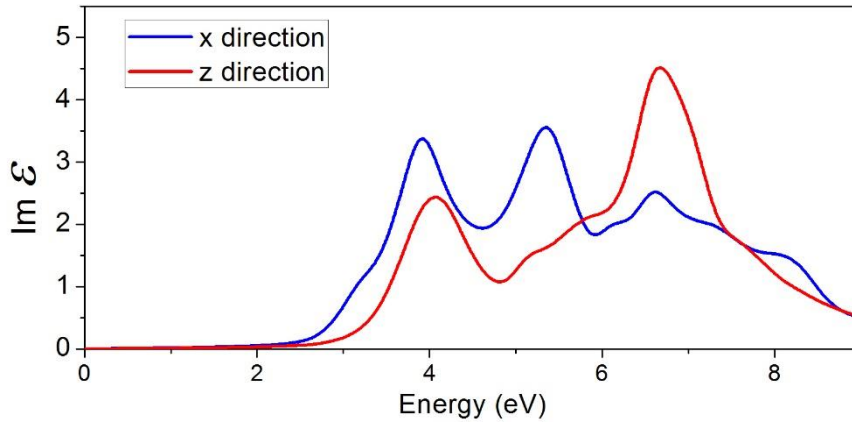
Figure S2. The imaginary part of dielectric function of monolayer CdI$_2$.

The imaginary part of dielectric function and light absorption (Fig. S2) indicate good absorption in solar light. Our results are in good consistence with previous works except for an energy shift due to the underestimation of GGA-PBE functional. CdI$_2$ thin film is reported by experimental works to has a direct optical energy gap of ~3.5 eV which seems too large for photocatalysis. It is indicated by our results and previous experimental works that CdI$_2$ exhibit good absorption in ultraviolet lights and has great potential in photocatalysis. Efficient ways to modulate its band edges are desired to improve the optoelectronic properties and photocatalytic activity.
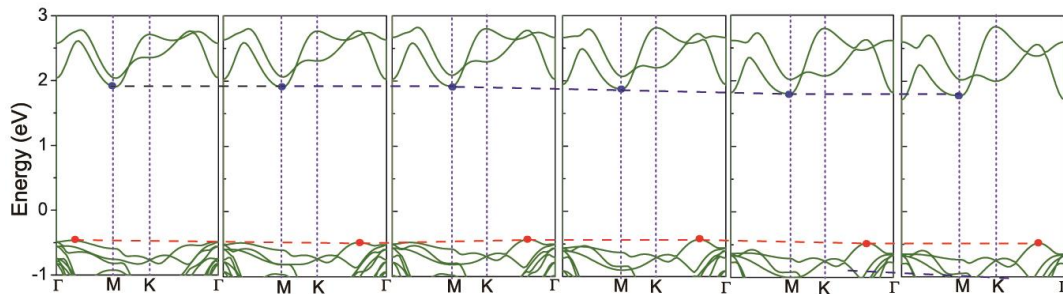

Figure S3. Evolution of band structure of bilayer CdI$_2$ as a function of applied normal press. The Fermi level is taken as reference. Variations of band edges (the VBM and CBM) are plotted by blue and red line, respectively.

The band structures of bilayer CdI$_2$ under different normal press are show in Figure S2. Different with Figure 2d in the manuscript, the Fermi level is taken as reference here. Our results reveal that the band gap of bilayer CdI$_2$ decreases with the applied normal press with the CBM approaching the Fermi level and the VBM hardly chang.
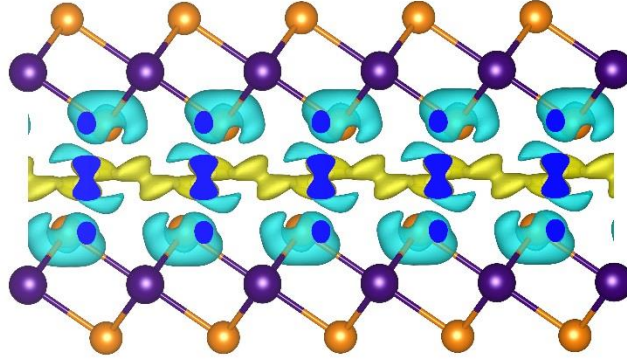
Figure S4. The charge density difference of bilayer CdI_2 without normal press or vertical electric field. The light blue and brown denote the isosurfaces of charge accumulation and depletion, respectively. The accuracy of the isosurfaces is set as 6×10^{-5} e

To determine the interlayer coupling between layers in CdI_2, binding energy of bilayer CdI_2 is calculated as

$$E_b = E_{bilayer} - E_1 - E_2$$

where $E_{bilayer}$, E_1 and E_2 are the total energy of bilayer form, first layer and second layer. The calculated E_b of bilayer CdI_2 is about 0.25 eV. The rather low binding energy indicates the weak van der Waals interlayer coupling. Similar evidence also comes from the charge density difference of CdI_2 bilayer, as shown in Figure S3. The charge density difference is calculated as the difference between the charge density of bilayer and the sum of charge density of two monolayers. It is found that a slight of charge transferring occurs between the layers upon binding together.
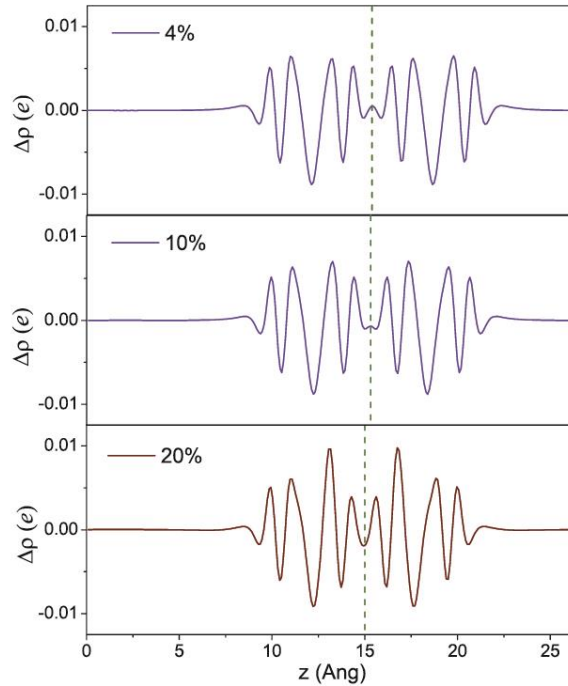

Figure S5. The integrated charge density difference of bilayer CdI_2 under different applied normal press.

To determine the effect of applied normal press on the electronic structure of bilayer

CdI$_2$, the integrated charge density difference in CdI$_2$ bilayer under different normal press is calculated in Figure S4 as,

$$\Delta\rho_\varepsilon(z) = \int \rho_\varepsilon(x,y,z)dxdy - \int \rho_1(x,y,z)dxdy - \int \rho_2(x,y,z)dxdy$$

where $\rho_\varepsilon(x,y,z)$ is the charge density at the (x,y,z) point of bilayer under the applied normal press ε. $\rho_1(x,y,z)$ and $\rho_2(x,y,z)$ are the charge density at the (x,y,z) point of first-layer and second-layer CdI$_2$ without applied press. Our results reveal that increasing amount of charge transfer is brought about by increasing applied normal press. The enhanced interlayer coupling results in the change in the electronic structure of bilayer CdI$_2$. Specifically, band gap of CdI$_2$ bilayer is reduced by applied normal press with the CBM and VBM exhibit the varying trend shown in Figure S2.
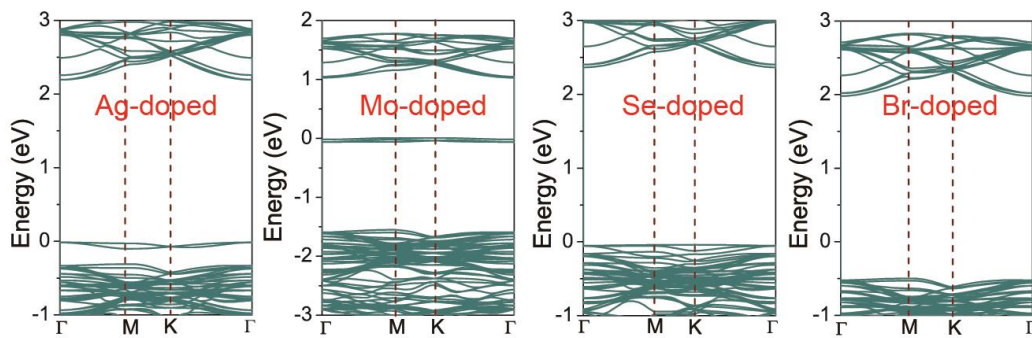

Figure S6. Band structures of doped CdI$_2$ monolayer. The Fermi level is taken as reference.