Fig. S1. The geometries of original h-BN (a), p-BN (b), 2×2×1 supercell of p-BN (c), and defect p-BN (d).
Fig. S2. The geometric configuration and total density of states (TDOS) of perfect p-BN.
Fig. S3. The geometric configurations for nonbonding: (a) perfect p-BN and Cr(III), (b) V₄ and Cr(II), and (c) V₂ and Cr(III).
Fig. S4. The total density of states (TDOS) for Cr(III) adsorbed on perfect p-BN (a), V_N (b) and V_B (c) from DFT and DFT+U methods.

The projected density of states (PDOS) for Cr(III) adsorbed on perfect p-BN (d), V_N (e) and V_B (f) from DFT+U. Dashed line denotes the position of the Fermi level.
S1 computational details

The formation energies ($E_{\text{form}}$) of (Cr(III))$_2$/Cr(VI)$_2$ adsorbed on p-BN with V$_B$ or V$_N$ defect were calculated using the following formula:\textsuperscript{1-3}

$$E_{\text{form}} = E_{\text{tot}} - E_{\text{BN}} - n_{\text{Cr}} \mu_{\text{Cr}}$$ \hfill (S1)

where $E_{\text{tot}}$ is the total energy of Cr ions adsorbed on p-BN with V$_B$ or V$_N$ defect. $E_{\text{BN}}$ is the energy of p-BN with V$_B$ or V$_N$ defect. $n_{\text{Cr}}$ is the numbers of the Cr ions. We consider the energetic stability of (Cr(III))$_2$/Cr(VI)$_2$ cluster, relative to Cr atoms and $\mu_{\text{Cr}}$ is obtained from Cr atom in the gas phase.
Table S1. The formation energies ($E_{\text{form}}$/eV) of the Cr ions on p-BN with $V_B$ and $V_N$.

<table>
<thead>
<tr>
<th>$E_{\text{form}}$/eV</th>
<th>(Cr$^{3+}$)$_2$/VN</th>
<th>(Cr$^{3+}$)$_2$/VB</th>
<th>(Cr$^{6+}$)$_2$/VN</th>
<th>(Cr$^{6+}$)$_2$/VB</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.10</td>
<td>9.69</td>
<td>4.37</td>
<td>11.23</td>
<td></td>
</tr>
</tbody>
</table>
References