Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary for "Band gap reduction in van der Waals layered 2D materials via de-charge transfer mechanism"

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1. TB fitting within the third nearest-neighbor hopping for C_3N monolayer

Considering only the nearest-neighbor (NN) hopping, the TB bands for C_3N monolayer is not as good compared to the HSE bands, the non-dispersive band along Γ-M is different from the HSE results (see Fig. S1(b)). The lattice of C_3N can be considered as a 2×2 supercell of graphene, so that the band folding is responsible for the flat band along Γ-M when considering only the NN hopping. Improvement can be readily made by including high-order hopping. The TB bands with up to the third NN hopping in shown in Fig. S1 (a) which agrees much better with the HSE bands.

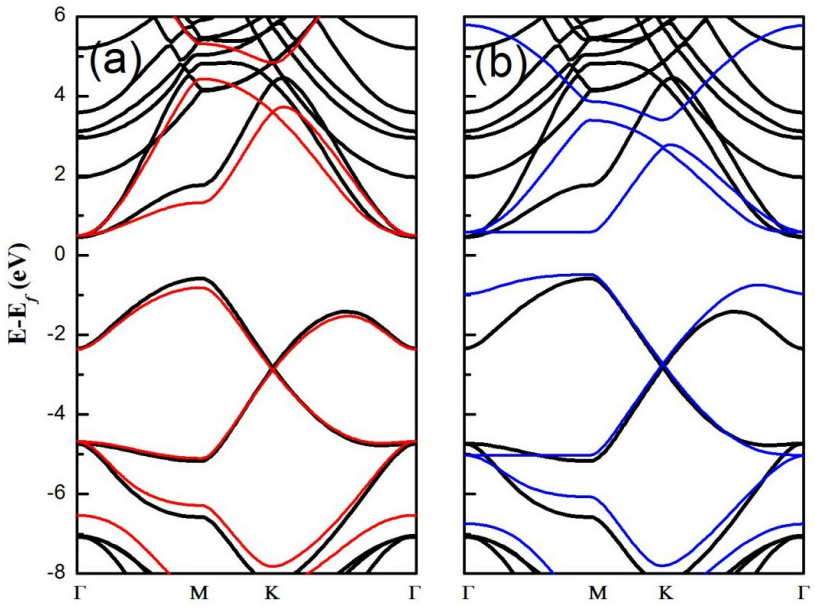

Fig. S1 TB fitting (red lines) with (a) the third NN hopping and (b) the NN hopping.

The detailed TB fitting parameters are: the on-site energies ϵ_C = -2.92 and ϵ_N = -5.4, the 1NN hopping C-C_1st = -3.5 and C-N_1st = -3.3, the 2NN hopping C-C_2nd = -0.4 and C-N_2nd= -0.28, and the 3NN hopping C-C_3rd = -0.32 and N-N_3rd = -0.35.

2. The stability of C_3N bilayer

Before studying the band structure of C_3N bilayer, we have investigated the stability of C_3N bilayer in details. We considered different stacking patterns and found the four most relatively stables structure, as shown in Fig. S2. The binding energy, defined as the energy difference between C_3N bilayer and two isolated C_3N

monolayer, is given in Table S1. One can see that the AD stacking is the most stable configuration for C_3N bilayer.

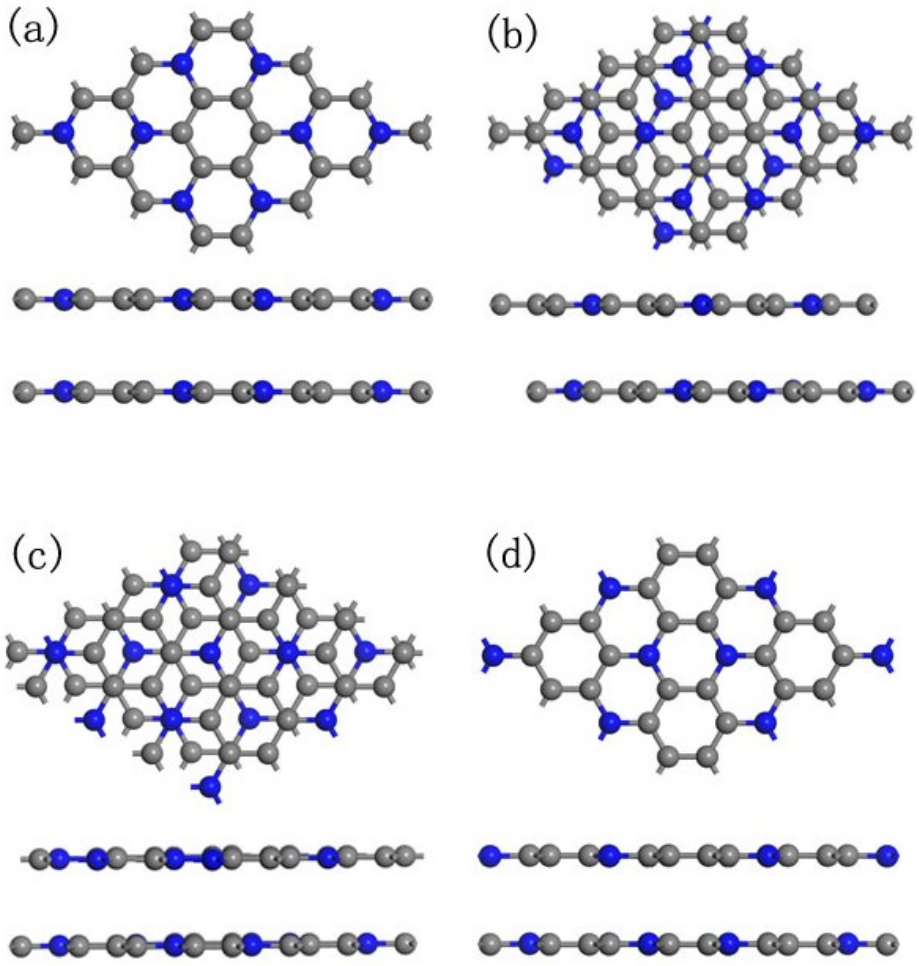

Fig. S2 Four stacking structures of C_3N bilayer, (a)-(d) Top view and side view of AA-, AB-, AC-and AD-stacking, respectively. A 2×2 super cell is adopted for the view. Grey (blue) ball denotes carbon (nitrogen) atom.

Table S1 The interlayer distance and binding energy of C_3N bilayer with different stackings.

Stacking	Interlayer distance (Å)	Binding Energy(eV/unit cell)
AA	3.341	-0.359
AB	3.163	-0.426
AC	3.170	-0.420
AD	3.175	-0.428