Supplementary Information Introducing novel electronic and magnetic properties in C₃N nanosheet by defect engineering and atom substitution

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To provide visible guidance for experimental observations, simulated STM images of SV_C , SV_N , DV_{CC} , DV_{NC} , DV_{NN} , AS_{NC} , SW_{CC} and SW_{NC} defects are shown in Fig. S1(a-h). The STM image is overlayered with the C₃N lattice with carbon (gray ball) and nitrogen (blue ball) atoms. The total charge density is also shown as the little inset figures. The blue region represent charge accumulation. From the STM images of C₃N at +2.0 V bias, it is easy to recognize the C₃N atomic structure. From the STM image, the SV_C dangling bonds are shown by the one spot missing in the asymmetric spots array. In the image, atoms around the defective site show up as bright spots. The STM images corresponding to SV show very bright spots, suggesting a strongly localized electronic density around the SV defects. In addition, the DV are easy to distinguish in the positive bias STM image, by the bright spots around the defect region. For SW, one defect is surrounded by a hexagonal ring, and the other is located at the pentagonal and heptagonal ring. The one surrounded



Figure 1: Simulated STM images of (a) SV_C , (b) SV_N , (c) C+C (DV_{CC}), (d) N+C (DV_{NC}), (e) N+N (DV_{NN}), (f) anti-site (AS_{NC}), (g) C-C (SW_{CC}) and (h) N-C (SW_{NC}) topological defects in C₃N. The total charge density are also shown. Where the blue regions represent charge accumulation.

by a hexagonal ring C atoms are brighter than the one surrounded by a pentagonal ring of N atoms with dark spots.

Next we consider the study of Li, Na, K, Be, Mg, Ca and Al atom substitution in C₃N. Optimized atomic structures with corresponding structural parameters including atomic bond length and bond angles, are shown in Figs. S2(a,b). In contrast to H, O, S, F, C, Si, N and P atoms, which cause only little distortions of the C₃N structure, substitution of Li, Na and K atoms, result in stronger distortion of the C₃N lattice. Such a substitution results in the occurrence of local deformations and even reconstructions of the C₃N lattice. From the optimized structures with Li, Na, and K atoms it is apparent that there is interaction through sp^2 -hybridization and the formulation of three σ bonds with the neighboring atoms. The bond lengths with the nearest N atoms are 1.648, 1.858 and 2.269 Å for Li, Na and K atoms, respectively, and a strong distortion of the planar structure of C₃N is observed. Also for Na_N and K_N interaction through sp^2 -hybridization and the formulation of three σ bonds



Figure 2: Optimized structures of the Li, Na, K, Be, Mg, Ca and Al substituted on (a) C and (b) N atom sites of C_3N . The corresponding, structural parameters including atomic bond length and bond angles are indicated.

with neighboring N atoms and the bond lengths with nearest N atoms are 2.987 and 3.058 Å. The bond angles are 119°, while, Li_N leads to the formulation of three σ bonds with the neighboring C atoms. The Li-C bond length is 1.594 Å and the bond angle is 119°. We found that the bond length increases when going from Li to Na, and to K. This is a direct consequence of the size of the substituted atoms. Because of the changes in the optimized structures, the charge transfer between the substituted atoms and the substrate is slightly different from the expected value from the non-interacting atom. Considering Be_C, Mg_C and Al_C, we notice that they interact through sp^2 -hybridization and form three σ bonds with the neighboring N and C atoms. The bond length of these substituted atoms and the N (C) atom are 1.541 (1.608), 1.796 (1.849), and 1.724 (1.766) Å, and the bond angles are found to be in the range of 111°-119°. While Ca_C forms three σ bonds with the neighboring three N atoms and the bond lengths with the N atoms are 2.015 and 2.838 Å. In the case



Figure 3: DOS and PDOS of Li, Na, K, Be, Mg, Ca and Al substituted of (a) C and (b) N atom sites of the C₃N. Difference spin density distribution are shown in the inset. The blue and yellow colors show the \uparrow and \downarrow spin directions. The zero of energy is set to E_F , shown by the green dash-point line.

of substitution of the C atom we have 1.445, 1.796 and 1.724 Å and the bond angles are in the range of $111^{\circ}-119^{\circ}$. For Sb-C₃N, the bond angles increase monotonically from Be to Al. There is electron accumulation on the Be atom and thus charge transfer from C₃N to Be takes place. According to the Mulliken charge transfer analysis, Li_C and Li_N, respectively, gain 0.169 e and 0.424 e charge from C₃N, while Mg and Ca donate a significant amount of electronic charge to C₃N.

DOS and PDOS for Li, Na and K atoms substituted are shown in Figs. S3(a,b). From DOS and PDOS, we see that the VBM of Na_N and K_N is due to the hybridization of Li/Na $p_{x,y}$ with C- $p_{x,y}$ and N- p_z orbitals of the nearest atoms, and the CBM is due to the C/N- p_z orbitals of the nearest C atoms. Since, in Ca_C, the DOS of the \uparrow and \downarrow spin states are not compensated there is a magnetic moment of 1.3 μ_B along with metallic properties. It is also



Figure 4: Simulated STM images of C (top figure) and (bottom figure) substituted with Si, Na and Mg atoms. Insets, represents optimized structures and the total charge density. The blue regions represent the charge accumulation.

seen that the VBM of Ca_C forms due to the hybridization of Ca-s orbital with p_z orbitals of the nearest N atoms, and the CB of Ca_C is due to the hybridization of Ca-s orbital with $C-p_z$ orbitals of the nearest C atoms. Whereas Ca_N is a half-metal with 1 μ_B magnetic moment and the VBM is due to the hybridization of Ca-s orbital with $C-p_{x,y}$ and $N-p_z$ orbitals of the nearest N atoms, and the CBM is due to the hybridization of Ca-s orbital with $N-p_{x,y}$ orbitals of the nearest N atoms. We continue our exploration with Mg_C and Mg_N , that are metallic and ferromagnetic-metal, respectively. The DOS of these structures is different from that of C_3N , displaying an impurity state around the Fermi level. Based on the calculated PDOS, for Mg_C the CBM and VBM receive contributions mainly from the hybridization of the $C/N-p_z$ orbitals, while Mg_N , comes from $Mg-p_{x,y}$ and $N-p_z$. To further elucidate the origin of magnetism, the difference spin density distribution of Na_C , Li_N , Na_N and K_N , are shown as inset in Figs. S3(a,b). The blue and yellow colors show the \uparrow and \downarrow spin directions. We found that the magnetism of these structures results from the Na, Li and K atoms and partly from the neighbor C and N atoms. For clarity of the spin arrangement on each atom we show in the inset also, the difference spin density distribution. We found that the magnetic moment of the Ca_N results from neighbor C and N atoms.

Simulated STM images of F, Si, Na and Mg substitution in C_3N of C (top figure) and (bottom figure) as discussed above, are shown in Figs. S4(a,b). The same set of simulation parameters was used for all the structures investigated. In STM images clear bright and dark spots are apparent, which stand for the relatively high and low locations, respectively. The STM image of F, Si, Na and Mg atoms can be easily distinguished as very bright spots which gives evidence for strongly localized electronic density around the substituting atoms.