Electronic Structure of Graphene/TiO$_2$ Interface: Design and Functional Perspectives

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We propose the design of low strained and energetically favourable mono and bilayer graphene overlayer on anatase TiO$_2$ (001) surface and examined the electronic structure of the interface with the aid of the first principles calculations. In the absence of hybridization between surface TiO$_2$ and graphene states, dipolar fluctuations govern the minor charge transfer across the interface. As a consequence both the substrate and the overlayer maintain their pristine electronic structure. The interface with monolayer graphene retains its gapless linear band dispersion irrespective of the induced epitaxial strain. The potential gradient opens up a few meV bandgap in the case of Bernal stacking and strengthens the interpenetration of the Dirac cones in the case of hexagonal stacking of the bilayer graphene. The difference between the macroscopic average potential of the TiO$_2$ and graphene layer(s) in the heterostructure lie in the range 3 to 3.13 eV which is very close to the TiO$_2$ bandgap of 3.2 eV. Therefore, the proposed heterostructure will exhibit enhanced photo-induced charge transfer and the graphene component of it serves as a visible light sensitizer. Together these two phenomena make the heterostructure promising for photovoltaic applications.

I. INTRODUCTION

Owing to superior carrier mobility, large surface area, high strength and unique electronic properties, graphene has been extensively investigated for fabricating nanocomposites with semiconducting materials such as TiO$_2$, ZnO and SnO$_2$, etc. [1–8]. The resultant heterostructures show better efficiency in photocatalysis and photovoltaic applications due to enhanced charge carrier separation and shift in the absorbance spectra to visible region [3–5, 9–12]. Among the semiconductors, anatase TiO$_2$ is still the most preferred material for photocatalytic and photovoltaic applications due to its chemical stability, greater photo-corrosion resistance, and suitable electronic band edge positions [13–15]. Therefore, the electronic structure study of the graphene-TiO$_2$ (G/TiO$_2$) interface holds significance from both fundamental and applied perspectives.

Functionalization of monolayer or bilayer graphene is also equally significant from the application point of view [16–17]. For example, inducing a bandgap in this zero bandgap semiconductor has remained an open issue [18–20]. In the present context, the bandgap opening is important for absorption of light, which may help in photocatalytic/photovoltaic applications. In fact, there are a number of first principle electronic structure calculations that have reported graphene as an overlayer on anatase TiO$_2$(001) surface leads to a finite bandgap of 0.45–0.65 eV [21–23]. Interestingly, similar calculations report that the graphene does not exhibit any bandgap when it becomes an overlayer on other surfaces such as anatase(101) [24, 25] and rutile(110) [26–28]. Therefore, it raises two valid possibilities. Firstly, the anatase(001) surface may be inducing large epitaxial strain on the graphene layer as through effective π-band model. Theoretically, it is reported that a band gap opens up when a monolayer graphene is uniaxially strained along the zigzag direction with a strain above 26% [29], or with the application of a shear strain above 16% [30]. Also, it is reported that an anisotropic strain with a combination of a -20% compression in the armchair direction and 11% stretching in the zigzag direction can yield a bandgap in graphene [31]. Secondly, there may be strong chemical bonding between graphene and TiO$_2$ which lead to breakdown of the characteristics Dirac π bands.

Furthermore, the charge transfer mechanism at the graphene-anatase TiO$_2$ (G/A(001)) interface remains a matter of intense investigation because of its influence on potential applications in the area of photocatalytic and photovoltaic processes [6, 16, 19, 25, 32]. An experimental photoluminescence (PL) spectroscopy study carried out on a multilayer of hybrid films made up of alternate graphene and titania nanosheets has reported that the transfer of photo-excited electrons from graphene to titania layers is faster than the average excited state carrier lifetime for graphene with measured electron transfer time scales of the order of 200–250 fs [35]. This observation is also supported theoretically, in the case of graphene/rutile(110) interface, using non-adiabatic MD (NAMD) simulations where the photoexcited electron transfer is reported to be several times faster than the electron-phonon energy relaxations [27]. Similar results on charge transfer from C-p to Ti-3d states have also been reported for G/A(101) [18, 24, 25] and G/R(110) interfaces [26, 28]. Irrespective of the orientation of the surface, it is expected that similar kind of charge transfer should occur for G/A(001) interface as well. However, it is reported that the charge transfer takes place from anatase (001) surface to graphene [21, 22].

In the present study, the electronic structure and stability of the anatase TiO$_2$ (001)-graphene interface is examined through density functional calculations, and an energetically favorable low strained graphene overlayer is
proposed. The analysis of the electronic structure reveals that in the absence of chemical bonding, the heterostructure is stabilized through van der Waals interaction and as a consequence, both the substrate and the overlayer retain their pristine electronic structure. The dipolar fluctuation is also responsible for minor charge transfer just across the interface and in the case of bilayer graphene, it leads to a potential gradient between the upper and lower carbon layers. This results in opening up a narrow bandgap to the tune of ~ 80 meV in the case AB stacked bilayer graphene. The difference in macroscopic potential average across the graphene and TiO₂ is found to be close to the bandgap of TiO₂ which makes the graphene Dirac point to be in resonance with the TiO₂ conduction band. This felicitates the photo-induced charge transfer and makes the heterostructure promising for photovoltaic applications. The earlier report of wide band gap opening in G/A(001) interface is reexamined and through a detailed analysis of the band dispersion in the full Brillouin zone reveals that a monolayer graphene as an overlayer cannot open a bandgap irrespective of the strain induced by the host TiO₂.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

The \textit{ab initio} electronic structure calculations are performed using plane wave based pseudopotential approximations and PBE-GGA exchange-correlation functional as implemented in Quantum Espresso. The ion-electron interactions are expressed through ultrasoft pseudopotential. The electron wave functions are expanded using plane-wave basis sets with a kinetic energy cutoff of 30 Ry and an augmented charge density cutoff of 300 Ry. The dispersion corrections have been included through the semi-empirical Grimme-D2 van der Waal’s correction. The calculated lattice parameters of anatase in bulk phase are \( a = 3.794 \) Å, \( c = 9.754 \) Å which agree well with the previously reported experimental and theoretical values. The anatase (001) surface is created using slab geometry with four TiO₂ layers (thickness \( \sim 8.5 \) Å) which is observed to be sufficiently thick enough and a 15 Å vacuum along the out-of-plane direction. The optimizations are performed using a \( 4 \times 4 \times 1 \) Monkhorst-Pack k-mesh with force convergence criteria set to be 0.025 eV/Å. During the relaxation, only the upper two layers are allowed to move freely, whereas the atoms in the bottom two layers are fixed to their bulk positions. For the electronic structure calculation, the Brillouin zone integration is carried out on a finer grid of \( 8 \times 8 \times 1 \) k-mesh. To calculate the electronic structure of pristine and strained graphene unit cell, a denser k-mesh of \( 60 \times 60 \times 1 \) is considered as it is found that the Dirac point is very sensitive to the strain and identification of it requires a finer k-mesh. The structural models and iso-surface charge density plots are made using VESTA.

III. RESULTS AND DISCUSSIONS

A. Design of G/A(001) interface

The key to design a low-strain G/A(001) interface lies in patterning the graphene layer on TiO₂(001) surface as shown in Fig. 1. In the conventional method, as followed in earlier works, a rectangular unit cell is created out of the regular hexagonal graphene unit as shown in Fig. 1(b). A supercell of desired size to commensurate with the A(001) surface is then created out

\[
\varepsilon = \sqrt{\frac{\epsilon_{xx}^2 + \epsilon_{yy}^2 + 2\epsilon_{xy}}{4}},
\]

where \( \epsilon_{xx}, \epsilon_{yy}, \) and \( \epsilon_{xy} \) are the components of the 2D strain tensor. These components are expressed through primitive surface lattice vectors \( (a_{1,x}, a_{1,y}) \) and \( (a_{2,x} \) and \( a_{2,y}) \) of TiO₂ and primitive lattice vectors of graphene \( (b_{1,x}, b_{1,y}), \) and \( (b_{2,x}, b_{2,y}) \) as follows.

\[
\begin{align*}
\epsilon_{xx} &= \frac{a_{1,x} - b_{1,x}}{b_{1,x}}, \\
\epsilon_{yy} &= \frac{a_{1,y} - b_{1,y}}{b_{1,y}}, \\
\epsilon_{xy} &= \frac{1}{2} \frac{b_{2,x}a_{1,x} - b_{1,x}a_{2,x}}{a_{1,x}a_{2,y}}.
\end{align*}
\]

The binding between the graphene layer and A(001) surface is quantitatively measured through the adhesion energy given by the following expression.

\[
E_{ad} = E_{G/A(001)} - E_{A(001)} - E_G,
\]

where, \( E_{G/A(001)} \) is the total energy of the optimized G/A(001) composite. \( E_{A(001)} \) and \( E_G \) represent the total energy of pristine A(001) surface and the graphene layer, respectively.

The other way to analyze the interaction between graphene and the A(001) surface is through the charge redistribution that takes place across the interface. It is measured through the three-dimensional charge density difference of G/A(001) composite estimated by the following formula.

\[
\Delta \rho(r) = \rho_{G/A(001)}(r) - \rho_{A(001)}(r) - \rho_G(r),
\]

where, \( \rho_{G/A(001)} \) represents the charge density of G/A(001) composite; while \( \rho_{A(001)} \) and \( \rho_G \) represent the charge densities of pristine A(001) surface and graphene layer, respectively.
FIG. 1. Construction of the interface between anatase TiO$_2$ (001) surface and graphene. (a) A 4×2 A(001) slab with in-plane lattice translation vectors ($\vec{a}_1$ and $\vec{a}_2$); (b) transformation of graphene unit cell from hexagonal to rectangular cell; (c) the composite structure G/A(001) interface for which the strain values on graphene are +2.82 % and -10.94 % along $\hat{x}$ and $\hat{y}$-directions, respectively. The rectangular unitcell of graphene is used in the previous works\[21, 23\] or in the design of G/R(110) interface\[26, 28\]. (d) The coherent lattice vectors for A(001) surface for which angle is 63.43 $^\circ$ with a supercell size of $2\sqrt{5} \times 2$ having 24 Ti and 48 O atoms in a four layered TiO$_2$ slab. (e) Rotation of graphene unit cell from 60 $^\circ$ to 63.4 $^\circ$. (f) The optimized structure of graphene layer with a supercell size of 7 × 3 on the A(001) surface. The average strain in this case is calculated to be $\sim$ 1.54%.

of this unit cell and laid over the TiO$_2$ surface to create the composite structure (Fig. 1(c)). However, the lattice matching needs strain to be applied along the zigzag and armchair directions of the graphene layer. The magnitude of the strain depends on the size of the surface area. A Similar formalism has been considered for G/R(110) interface\[26, 28\].

In this section, we present a scheme to define various low strained interfaces by designing new commensurate unit cells for the graphene layer whose vectors are given as:

$$\begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix} = \begin{pmatrix} m \alpha \alpha_n \\ 0 \ 2a \end{pmatrix} \begin{pmatrix} \hat{x} \\ \hat{y} \end{pmatrix}$$  \hspace{1cm} (5)

where, $a$ is the lattice parameter of A(001) slab in the $xy$-plane, $m$ and $n$ are integers, $\Theta = \angle \vec{a}_1 \vec{a}_2$. Depending on the values of $m$ and $n$, the angle ($\Theta$) between the lattice vectors $\vec{a}_1$ and $\vec{a}_2$ of A(001) surface varies. Few selected ($m$, $n$) pairs and corresponding $\Theta$ are listed in Table I. The table also lists the size of commensurate TiO$_2$ surface unit cells, size of the graphene supercell, total number of atoms in the composite considering a four layers of TiO$_2$ slab, the lattice mismatch, average strain as obtained from Eq. 1. The vector $\vec{a}_2^*$ is fixed with a length of 2$a$ (= 7.59 Å) as that accommodates almost three primitive unitcells of graphene (3$a_{\text{graphene}}$ = 7.38 Å) and the lattice mismatch is $\sim$ 2.82 %. For the case of $\Theta = 90^\circ$, we show that by simply increasing the surface area, one can reduce the average strain as it gives the flexibility to find out an ideal supercell of the rectangular graphene unit so that a matching area of the graphene can be obtained. However, despite there is a good matching among the supercell, the local strain at the unitcell range will persist. Furthermore, large surface area leads to large number of atoms in the composite structural unit, which in turn makes it computationally very expensive.

We examined several possible values of $\Theta$ and found that the case of $\Theta$= 63.4° represent minimum lattice mismatch of 1.54 %. The other designs are presented in the Appendix A. Also, the composite unit with $\Theta$ = 63.4° forms a natural construct for graphene as it is close to angle between the primitive lattice vectors of the pristine graphene. The resultant G/A(001) interface is shown in
TABLE I. The unit cell construction: The commensurate unit cell between A(001) surface and graphene layer along with the lattice mismatch. The negative and positive signs in lattice mismatch stand for compression and elongation of graphene. Here, we have considered a four layered TiO$_2$ lattice mismatch. The negative and positive signs in lattice mismatch stand for compression and elongation of graphene. Here, we have considered a four layered TiO$_2$.

| m | n | Angle $\Theta$ | $\Lambda$(001) supercell $a$ | Graphene supercell $a$ | Total no. of atoms | Lattice mismatch x (%) | y (%) | Strain $\epsilon$ | $E_{ad}$ (eV/C atom) |
|---|---|---|---|---|---|---|---|---|---|
| 4 | 0 | 90 | 4 $\times$ 2 | 6 $\times$ 2$^a$ | 144 | +2.82 | -10.94 | 4.59 | -0.041 |
| 4 | 0 | 90 | 4 $\times$ 8 | 6 $\times$ 7$^a$ | 552 | +2.82 | +1.78 | |
| 6 | 0 | 90 | 6 $\times$ 6 | 9 $\times$ 5$^a$ | 612 | +2.82 | +6.87 | |
| 5 | 2 | 68 $\sqrt{26}$ $\times$ 2 | 7 $\times$ 3 | 168 | -0.01 | +6.98 | 7.29 | -0.033 |
| 4 | 2 | 63.4 $\sqrt{25}$ $\times$ 2 | 7 $\times$ 3$^b$ | 138 | +1.78 | +2.84 | 1.54 | -0.049 |

$^a$rectangular graphene unit cell with lattice parameters $b_1 = 2.46$ Å and $b_2 = 4.26$ Å.

$^b$hexagonal graphene unit cell with lattice parameter $b = 2.46$ Å.

In addition to the applied strain, stability plays a major role in forming the interface. In the case of heterostructures, the stability is estimated through the adhesion energy calculation as given in the Eq. [3] We find that the adhesion strength of the proposed low strained interface is better than the conventional designs.

B. Electronic structure of the low strained G/A(001) interface

The electronic structure of the low strained G/A(001) interface is examined through calculation of the band dispersion, densities of the states (DOS), charge transfer across the interface and average potentials. The bands and DOS are shown in Fig. 2. The band structure of the heterostructure (Fig. 2(a)) is found to be almost a superposition of the band structures of TiO$_2$ slab (Fig. 2(b)) and the isolated strained graphene layer (Fig. 2(c)). Therefore, we draw the following two important conclusions. Firstly, the Dirac band dispersion is unperturbed due to the formation of the interface. Secondly, the chemical bonding is either negligible or absent and hence, most likely the van der Waal interactions emerging out of the fluctuating dipoles stabilize the interface. To examine the effect of strain on the graphene, we compared its band structure with that of the pristine graphene calculated using a 7×3 supercell (see Fig. 2(d)). The down-folding of the bands with the shrink in the Brillouin Zone leads to a shift in the Dirac point and now it lies along the path Γ-X. The strain, which is compressive along one of the lattice vector and expansive along the other, brings the Dirac point more close to X. This is likely due to strengthening of the p$_z$-p$_z$ bond along one direction and weakening along the other. Figure 2(e) shows the iso-contours of the band on the k$_x$-k$_y$ plane showing $\Lambda_1$ and $\Lambda_2$ forming two Dirac valleys as $K$ and $K'$ in the conventional hexagonal unit cell.

The interface phenomena is further examined by calculating the charge transfer across the interface. Figure 3(b) presents the planar-averaged charge density difference along the slab direction Z. The observations made from this figure are as follows. First, the inner layers of the TiO$_2$ slab hardly take part in the interaction and the charge redistribution takes place at the G/A(001) interfacial region. Second, it shows that the electrons are transferred from the graphene layer to the TiO$_2$ (001) surface which is opposite to what the earlier works on G/A(001) reported [21,23]. But this observation is in line with the previous works carried out for G/A(101) [25] and G/R(110) [25,27] interfaces. Third, the magnitude of charge transfer is small (of the order 10$^{-4}$ e/Å$^3$) which further reconfirms the absence of ionic or chemical bonding, and only a weak van der Waal coupling stabilizes between the G and A(001) surface. For getting a clear picture of this interfacial charge transfer, we have plotted the three-dimensional charge density difference calculated using Eq. 4 in Fig. 3(b). The yellow and cyan color lobes represent the charge accumulation and depletion regions respectively. It is clearly observed that the interaction between C-p and O-p states occur through p$_z$ orbitals.

C. Electronic Structure of the Reported Composites: The missing Dirac Point

While we proposed a low strained interface where no bandgap emerges, there are earlier literature reporting a bandgap as large as 0.59 eV in the G/A(001) interface [21,23]. Therefore, it is prudent to examine if a bandgap can be opened in the G/A(001) interface. For this purpose, we have taken the example of the interface proposed by Gao et al. [21] which is designed out of a supercell of size 14.95 × 14.87 × 26.13 Å$^3$. In terms of unit cells, it is formed out of a 7 × 6 graphene layer and a four layered thick 4 Å (001) surface. The structure is further relaxed. However, to be consistent with the reported configuration, during the structural relaxation the bottom two layers are kept fixed and the graphene layer is maintained at a distance of 2.85 Å from the top of A(001) surface. Figure 4(a) and (b) shows the optimized structure of the G/A(001) interface. The graphene layer is strained as the C-C bond length increases to 1.47 Å and 1.44 Å along the zigzag and armchair directions, respectively. Whereas in TiO$_2$, the equatorial Ti–O bond
FIG. 2. (a) The band structure and the total density of states (DOS) along with the partial DOS of Ti-d, O-p and C-p orbitals at G/A(001) interface and (b) isolated A(001) slab. The total DOS is shown in gray shaded region. (c) The band structure of isolated graphene layer same as that of G/A(001) composite and (d) the band structure of a pristine 7×3 graphene layer. (e) The contour indicating a pair of low-energy Dirac cones at Λ₁ and Λ₂, whereas the other direction represent high-energy states.

FIG. 3. (a) The planar-averaged differential charge density ∆ρ(z) for the G/A(001), and (b) the 3D charge density difference plot for the G/A(001) calculated using Eq. 4. The yellow and cyan colors represent the charge accumulation and depletion regions, respectively. The iso-value is set to be 6×10⁻⁴ e/Å³.

is elongated on one side (2.11 Å) and compressed on the other (1.76 Å) as compared to the bulk value of 1.79 Å. The Brillouin zone (BZ) of the corresponding structure is shown in Fig. 4 (c). The Bulk BZ is artificial as the periodicity along (001) includes the slab plus the vacuum periodicity along mapping of bulk to surface Brillouin zone (BZ) and the high symmetry (HS) points in the reciprocal space for the G/A(001) is shown in Fig. 4 (c).

In Figure 4(d), we have shown the band structure along the k− path (see the green lines in Fig. 4(c)) used in the earlier study[21] and the band dispersion is very well reproduced and it gives a band gap of 0.59 eV. However, when a system is strained anisotropically, the geometry of the direct lattice space and hence the reciprocal space changes and in such cases, the paths connecting the high symmetry points not necessarily reveal the salient features of the band structure. Therefore, scanning the eigenstates in the entire Brillouin zone is needed and therefore, examining the densities of states (DOS) is a right approach. In Fig. 4 (e), we have shown the total DOS and it yields a zero bandgap. The calculation of partial DOS suggests that in the vicinity of the Fermi level, while the C-p states constitute the valence bands, both C-p and Ti-d states form the conduction band.

A concrete understanding of the band structure requires the examination of top of valence and bottom of conduction band and the orbital composition. Specifically, it is crucial to examine whether the graphene has lost its Dirac bands and the bands are now altered due to covalent interaction and/or the charge transfer with the host TiO₂ layer. For this we scanned the points around the high symmetry point X. This is because, if we consider a rectangular unit cell for graphene as shown in Fig.
we will examine the interfacial electronic structure of bilayer graphene, both with Bernal (AB) and hexagonal (AA) stacking, grown on the A(001) surface. The optimized structures and the resulted electronic structures are shown in Fig. 5. In the case of AB (AA) stacking, separation between the A(001) surface and the BLG is found to be 2.95 Å (2.92 Å), while the separation among the carbon layers is measured as 3.29 Å (3.51 Å) which is nearly same as in the case of freestanding BLG[41]. The bilayer overlayer is found to be stable and the binding energies are calculated to be -1.64 and -1.63 eV for the AB and AA stacking, respectively.

To understand the interaction among the bilayer graphene and TiO₂ surface, we have plotted the band structure of the heterostructures and compared with that of the pristine bilayer supercell as shown in Fig. 5(b-e). In the case of pristine system, the AA stacking shows interpenetrating of Dirac cones and the AB stacking gives rise to a zero bandgap semiconductor with parabolic conduction and valence bands touching each other at the Dirac point[41]. As in the case of monolayer graphene, in the present case also, the interfacial electronic structure is simply a combination of the electronic structure of TiO₂ and graphene. The electronic structure formed by the graphene overlayer resembles to that of the pristine bilayer graphene.

In Figure 6, we estimated the charge transfer across the
FIG. 5. (a) The optimized geometry of bilayer graphene overlayer in both hexagonal (AA) and Bernal (AB) stacking on TiO$_2$(001) surface. (b) The band structure of AA-stacked A(001) heterostructure, and (c) the band structure of pristine $7 \times 3$ supercell of AA-stacked bilayer. Similarly, the electronic structure for (d) AB-stacked A(001) heterostructure and (e) pristine $7 \times 3$ supercell of AB-stacked bilayer graphene. The inset shows the zoomed portion of the AB-stacked overlayer on A(001) surface.

FIG. 6. (a) The planar-averaged differential charge density $\Delta \rho(z)$ for the AB stacked bilayer graphene on TiO$_2$(001) surface, and (b) the 3D charge density difference plot. The yellow and cyan colors represent the charge accumulation and depletion regions, respectively. The iso-value is set to be $6 \times 10^{-4} \text{e/Å}^3$.

interface for the case of AB stacking, and found that the weak charge transfer, purely governed by the dipole fluctuations, occurs only between the bottom graphene layer and the surface layer of TiO$_2$. The induced dipolar field breaks the symmetry between the two graphene layers by creating a potential difference between them[42]. Both the substrate induced strain and the potential difference affect the band structure of the BLG in the vicinity of the Fermi surface as can be seen from the inset of Fig. 5(d). There are two pair of parabolic bands occupying the Fermi surface. The small hump in the conduction band and dip in the valence band at the high-symmetry point X is the result of the dipolar field and it leads to formation of a very small bandgap ($\sim 80$ meV). The charge transfer in the case of AA stacked bilayer graphene is nearly identical to the case of AB stacking and hence not shown here. However, since the electric field does not affect the linear dispersion of the bands in the AA bilayer graphene, the interpenetration of the Dirac cones remains unaffected as can be seen from Fig. 5(b).

The heterojunction potential leading to the band-offset between graphene and TiO$_2$ surface is examined by estimating the macroscopic average of the electrostatic potential as shown in Fig. 7(a) and (b). The TiO$_2$ surface lies at a higher electrostatic potential than the monolayer as well as bilayer graphene. The potential difference is calculated to be 3.04 eV and 3.13 eV for mono and bilayer graphene, respectively. A schematic of the charge transfer process at the G/TiO$_2$ surface is presented in Fig. 7(c). As the G/A(001) interface is a zero band gap system, it can absorb all wavelengths of light. When visible light incidents, electrons are excited in the graphene layer.
These excited electrons are in resonance with the TiO$_2$ conduction band and can move easily from C-p states to the Ti-d states in the conduction band. In this way, graphene acts as a visible light sensitizer as well as charge separator. A similar charge transfer mechanism has been reported for the interface formed out of graphene overlayer on rutile (110) and anatase (101) surface\textsuperscript{25–27}.

E. Effect of Strain

In the absence of a chemical bonding between the substrate and the graphene overlayer, the root question, now we need to address is that can strain alone open a bandgap in monolayer graphene? The theoretical model proposed earlier suggests that one can open a bandgap beyond $\sim 16\%$\textsuperscript{29} along zigzag direction or with a shear strain of $\sim 26\%$\textsuperscript{29} or with a shear strain of $\sim 16\%$\textsuperscript{43}. However, the model was restricted to the $\pi$-bands as generally it has been assumed that electronic structure of graphene is governed by the $\pi$-band and planar $\sigma$-bands has largely contributed towards the structural stability. In one the report, it has been found that defects and disorder can bring the $\sigma$ states close to the Fermi surface\textsuperscript{30}.

The strain can be applied both along armchair and zigzag direction. However, it has been conclusively shown that the strain along the armchair direction does not open a gap \textsuperscript{25–30}. Therefore, in this section we will represent the electronic structure of graphene with strain applied along the zigzag direction.

As a result of the applied strain, the lattice parameters gets modified as $a'_i = I(1+\epsilon)\cdot a_i$, where $I$ is the $2 \times 2$ unitary matrix, $a_i$ the unstrained lattice vector, and $\epsilon$ is the strain parameter\textsuperscript{44}. The associated reciprocal lattice vectors $b_i$ gets modified as $b'_i = (I + \epsilon)^{-1} \cdot b_i$.

The evolution of the band structure with increasing $\epsilon$ is shown in Fig. 8. With strain, the linear dispersion of the $\pi$-bands do not change. However, the point of crossing (Dirac point) of these bands gradually shifts. With strain, the points $K'$ and $K''$ gradually move towards $M$ and $M'$. With strain, while $K'$ no longer remains as a Dirac point as a gap opens up at this point. The Dirac points earlier located at $K$ and $K''$ are now shifted towards $M$ and $M'$. Beyond $\epsilon = 0.28$, a narrow bandgap opens up between the $\pi$ and $\pi^*$. The lower $\sigma^*$ band (red curve) which was lying far above the Fermi level is gradually pushed down with strain and above $\epsilon = 0.28$, it crosses the Fermi level at $M$ and $M'$ and therefore, there is no real bandgap in the system\textsuperscript{30}.

IV. CONCLUSION

To summarize and conclude, we have examined the interfacial electronic structure for the anatase TiO$_2$-graphene heterostructure grown along the (001) direction and proposed a low-strained and energetically favourable orientation for the graphene overlayer. In this design, the graphene almost retains the natural angle of $\pi/3$ between its two lattice vectors. In the absence of covalent bonding and ionic charge transfer, van der Waal interactions stabilizes the system. For the case of monolayer graphene, the electronic structure of the heterostructure is found to be a combination of the electronic structure of free TiO$_2$ and free graphene. Contrary to earlier reports the monolayer graphene(MLG) does not open a gap and the linear dispersion with the Dirac cones are maintained. We attributed this to the fact that in the absence of covalent bonding, the epitaxial strain induced by TiO$_2$ cannot open a bandgap in the MLG. The bilayer graphene (BLG) as overlayer reconstruct the Fermi surface. In this case, as dipolar fluctuation led charge transfer exists only between the surface of TiO$_2$ and bottom layer of the BLG, an electrostatic potential gradient is induced between the graphene layers. Both the epitaxial strain and the potential gradient are capable of creating a bandgap ($\sim 80$ meV) in the AB stacked BLG overlayer. Both MLG and BLG as provide an excellent platform for
photoinduced charge transfer from graphene to TiO$_2$ as the average potential difference between them is in the range 3.0 to 3.13 eV which is close to the TiO$_2$ bandgap of 3.2 eV. Therefore, anatase TiO$_2$(001)-graphene heterostructure is promising for photovoltaic applications.

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Appendix A: Design of G/A(001) interface as a function of G overlayer

As mentioned in the main text, by aligning the graphene overlayer at different angles (such as 90° and 68.19°) governed through m and n values of Eq. 5, we have created new commensurate unit cells as shown in Fig. 9. For Θ = 90°, the overlayer design is same as that of the rectangular pattern of graphene as shown in Fig. 9(a-c) of the main-text. The separation between the TiO$_2$ slab and graphene for this case is calculated to be 2.90Å (see Fig. 9(a) and (b)). The average value of strain calculated using Eq. 1 and the adhesion energy using Eq. 3 for this interface is estimated to be 4.6 % and -0.04 eV/C respectively. Similarly, for Θ = 68.19° the graphene overlayer lies at distance of ~3Å from the top of TiO$_2$ slab (Fig. 9(c) and (d)). The interfacial average strain is ~7.2 % and the adhesion energy of -0.03 eV/C. The electronic structure and PDOS in both the overlayer patterns show that the graphene retains its Dirac cone nature (Fig. 9(b) and (d)). The band re-positioning is due to the different strain values applied on graphene overlayer. The analysis follows as that discussed for Θ = 64.43° in the main-text.

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FIG. 9. Construction of G/A(001) interface as a function of graphene overlayer at different angles which are chosen from the angle made by the in-plane lattice translation vectors ($a_1$ and $a_2$) of A(001) surface. (a) Top view and side view of the G/A(001) interface at angle ($\Theta$) 90° and (b) its corresponding band structure and partial DOS along with the total DOS. Similarly, (c) shows the optimized structure at $\Theta = 68.19^\circ$ and (d) its band and partial DOS. The total DOS is shown in gray shaded region. The Fermi level is set to be zero.

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